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Statistics of « starburst » polymers

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Résumé. — Nous analysons la croissance d'un polymère *complètement ramifié*, basé sur des branchements amine tertiaire reliés par des segments flexibles de P monomères. La méthode est une version adaptée du champ « self consistent » de S. F. Edwards. Nous trouvons que la croissance en chou-fleur idéal (sans fonctions amine secondaire résiduelles) est limitée à un nombre de générations $m \leq m_1$ où $m_1 \sim 2,88(\ln P + 1,5)$. Ceci correspond à un rayon limite spatial R_1 linéaire en P . Bien en dessous de la limite, le rayon $R(M)$ varie avec la masse moléculaire M comme $M^{0,2}$. Au-delà de la limite on attend des structures compactes ($R \sim M^{0,33}$).

Abstract. — We discuss the growth of completely branched polymer, based on tertiary amine branch points connected by flexible linear portions (« spacers ») each of P monomers. The method is a modified version of the Edwards self consistent fields. We find that ideal « starburst » growth (without any residual secondary amine functions) is restricted to a number of generations $m \leq m_1$ where $m_1 \cong 2.88(\ln P + 1.5)$. This corresponds in space to a limiting radius R_1 which increases linearly with P . Well below this limit, the polymer radius $R(M)$, plotted as a function of molecular weight M , should increase like $M^{0.2}$. Above the limit ($R > R_1$) we expect compact structures ($R \sim M^{0.33}$).

1. Aims and methods.

Recently D. A. Tomalia *et al.* [1] have performed a sequential construction of branched polymers (Fig. 1) where (in principle) each generation (m) is fully reacted before proceeding to the next ($m + 1$). Within a few generations ($m \gtrsim 5$) this leads to a very compact object, with very little polydispersity, which they have called a « starburst » polymer⁽¹⁾. Typical molecular weights are of order 30,000, and the whole structure is reminiscent of a globular protein. Variants from this basic scheme may allow for rigid stereospecific sites near the surface, and may be of practical interest.

Our aim in the present note is much more modest, and purely theoretical : clearly the exponential growth described in figure 1 cannot persist indefinitely because of steric hindrance. Thus there must exist a limiting generation number (m_1) or radius (R_1), or molecular weight (M_1), beyond which the starburst structure becomes imperfect : not all the amine functions can be tertiary and certain secondary amine functions must be present. If the spacer is very short, one may estimate m_1 from a construction on a suitable periodic lattice, with coordination number 3 on each site. We are interested here in the opposite limit, where the spacer is relatively long, and flexible : for instance an aliphatic chain with a number P of carbon atoms. We expect that large P

⁽¹⁾ Some scientists prefer « Cauliflower Polymer ».

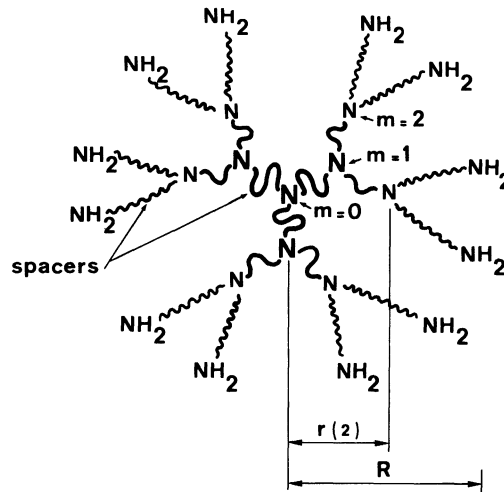


Fig. 1. — Chemical structure of a starburst molecule with 2 generations. In the structures realized by Tomalia *et al.* the spacer usually contains 4 aliphatic carbons and an amide group.

would allow for higher starburst limits M_1 , and we want to predict, at least qualitatively, the dependence of M_1 on P .

We also want to ascertain what is the structure of the starburst molecules below threshold ($M < M_1$); what is, for instance, their density profile $\phi(r)$. (Here ϕ is the local polymer fraction and r is the distance from the centre). We assume that :

- a) the solvent is very good (athermal);
- b) at each generation the system is fully reacted : no secondary amine functions present (we remove this restriction in the appendix);
- c) the spacers are long, so that the detailed structure of the bonds near any tertiary amine are not relevant. This is not fully achieved for the actual Tomalia systems, but is a natural starting point ;
- d) the cross links (N) are chemically not too different from the spacer (no strong segregation trends).

Physically, the main effect which we have in mind is the following : near the centre the spacers may behave like flexible coils, but in the outer region they must be elongated, thus allowing for an increased radius and preventing too high densities.

The two basic components of the free energy are then : a) an intermonomer repulsion ; b) the elasticity of the spacers. The competition between a) and b) can be treated very naturally by the Edwards self consistent field method [2]. Indeed, for these rather compact systems, the self consistent field approach should be unusually good. There are two numerical complications in our case :

- (i) the densities are high ($\phi \sim 1$) : the simplifications found in semi dilute solutions do not apply ;
- (ii) the spacers are strongly elongated : they cannot be described in terms of harmonic springs.

Both (i) and (ii) lead to consequences which are somewhat sensitive to the detailed structure of the chains. In the present work, we incorporate (i) through a Flory-Huggins structure for the entropy of mixing, and (ii) by assuming a freely jointed chain (P units of length a) for each spacer.

Fortunately, when we discuss the inner core of a starburst molecule we find that in this region $\phi(r)$ is still rather small and that the elongations are not too large : thus, for the core region, our results are relatively insensitive to the complications (i) and (ii).

2. Self consistent fields.

2.1 THE FORCE EQUATION. — Our starting point is the balance of forces displayed on figure 2. We consider one of the cross links belonging to the m -th generation at a distance $r(m)$ from the centre. This cross link is subjected to :

- an interaction force F , pointing inwards, due to the concentration gradient $d\phi/dr$,
- three elastic forces f_1, f_2, f_3 due to the 3 spacers which are attached to the cross link. All these forces are radial on the average.

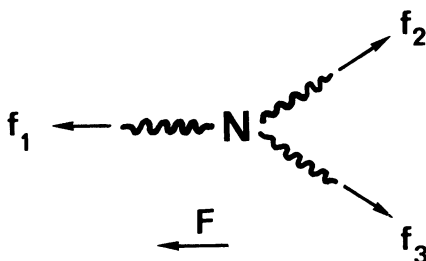


Fig. 2. — The balance of forces at one junction point inside the structure f_1, f_2, f_3 are elastic forces, while F is due to the concentration gradient.

We derive F from a Flory-Huggins form of the free energy f [3]. Our chains are inscribed on a cubic lattice of mesh size a (volume per monomer a^3). Since we assume an athermal solvent, we are left with only one contribution, from the entropy of mixing :

$$f|_{\text{site}} = kT(1 - \phi) \ln(1 - \phi) + \text{const.} \tag{1}$$

The free energy per spacer is Pf .

The resulting force per cross link is

$$F = - \frac{d}{dr} (2 P \mu) = - 2 P \frac{kT}{1 - \phi} \frac{d\phi}{dr}; \quad \left(\mu = \frac{\partial f}{\partial \phi} \right). \tag{2}$$

The factor $2 P$ expresses that, when we add one node, we add two spacers ⁽²⁾ : note the difference with a periodic lattice, where each node would be associated with $3 P/2$ monomers.

Let us now analyse the elastic forces. We shall first treat the spacers as harmonic springs (since this is easier to grasp) and later introduce the anharmonic corrections.

For a weakly elongated, freely jointed chain of P segments each of length a , with end points r_m and r_{m+1} , we have an elastic force

$$f_2 = f_3 = \frac{3 kT}{Pa^2} (r_{m+1} - r_m) \cong \frac{3 kT}{Pa^2} \frac{dr}{dm}, \tag{3}$$

where we neglect derivatives of order higher than d/dm . To this level we have $f_1 = - f_2$ and the total elastic force is simply

$$f_1 + f_2 + f_3 = \frac{3 kT}{Pa^2} \frac{dr}{dm}. \tag{4}$$

⁽²⁾ We ignore the difference between $2 P$ and $2 P + 1$, i.e. the junction volume.

(This is strikingly different from the Edwards equation for *linear* chains : in the linear case each node is subjected to *two* elastic forces only ; there is no contribution of order $\partial r/\partial m$, and the leading term is $\sim \partial^2 r/\partial m^2$.)

Let us now balance (4) against (2) : we obtain

$$\frac{3 kT}{Pa^2} \frac{dr}{dm} = F. \quad (5)$$

Finally, let us generalize equation (5) to strong deformations ($dr/dm \sim Pa$). For a freely jointed chain, the result can be written in terms of a Langevin function [4]

$$\mathfrak{L}(\lambda) \equiv \coth \lambda - \frac{1}{\lambda}, \quad (6)$$

$$\lambda = \frac{aF}{kT} = \frac{Pa}{1-\phi} \frac{d\phi}{dr}. \quad (7)$$

Equation (5) now takes the improved form

$$\frac{1}{Pa} \frac{dr}{dm} = \mathfrak{L}(\lambda). \quad (5')$$

Note that, since $\mathfrak{L}(\lambda) \leq 1$, the elongation dr/dm is always below it's value for complete stretching (Pa).

2.2 COUNTING GENERATIONS. — Let us call $\nu(m)$ the number of cross links achieved after m generations $\nu(m) = 3 \cdot 2^{m-1} + 1 \cong 3 \cdot 2^{m-1}$. Going to a continuous notation we may write

$$d\nu = (\ln 2) \nu dm = 4 \pi r^2 dr \phi(r)/(2 Pa^3), \quad (8)$$

$$2 Pa^3 \nu = \int_0^r \phi(r') 4 \pi r'^2 dr' = 4 \pi r^2 \frac{dr}{dm} \phi(r) (\ln 2)^{-1}. \quad (9)$$

We insert in (8) the form (5') for dr/dm , and differentiate both sides of (8) with respect to r , obtaining

$$(\ln 2) \phi(r) r^2 = \frac{d}{dr} [r^2 Pa \phi(r) \mathfrak{L}(\lambda)]. \quad (10)$$

Returning to the definition (7) of λ we see that a natural dimensionless variable is $\rho = r/(Pa)$, and we rewrite (10) in the form

$$\left. \begin{aligned} (\ln 2) \phi(\rho) &= \rho^{-2} \frac{d}{d\rho} [\rho^2 \phi \mathfrak{L}(\lambda)] \\ \lambda &= (1 - \phi)^{-1} \frac{d\phi}{d\rho} \end{aligned} \right\} \quad (11)$$

Equations (11) are the basic, non linear, equations for ideal starburst growth.

3. Results.

3.1 SCALING FORM OF THE LIMITING RADIUS. — The parameter P has dropped out of equations (11). As we shall see these equations lead to pure starburst growth for ρ smaller than a certain limit ρ_1 , which is a pure number $\rho_1 \cong 4$. Thus the limiting radius R_1 must be of the form

$$R_1 = (\text{const.}) Pa (\cong 5 Pa) \quad (12)$$

and is *proportional to the extended length* (Pa) of the spacers. (In Eq. (12) we have inserted the numerical value of the constant, derived from Eq. (21) below.)

3.2 BEHAVIOUR IN THE CORE REGION. — We consider first the region $\rho \ll \rho_1$: here, as we shall see, the polymer volume fraction $\phi(r)$ is much smaller than unity, and equations (11) may be reduced to a simpler form. Observing that $\mathfrak{L}(\lambda) \rightarrow \lambda/3$ for $\lambda \ll 1$ we get :

$$3 \ln 2 \phi(\rho) = \rho^{-2} \frac{d}{d\rho} \left[\rho^2 \phi \frac{d\phi}{d\rho} \right]. \quad (13)$$

This has the solution

$$\phi = \frac{3}{10} (\ln 2) \rho^2. \quad (14)$$

Thus we expect a parabolic density profile in the core region. It is natural to expect that ϕ be small at small ρ . Of course, the physical ϕ does not vanish exactly at the centre. This feature could be improved if we considered each generation (and in particular $m = 0$) separately, i.e. if we did not make the m variable continuous. But we expect the corrections to be important only in a region comparable to the coil size of an unstretched spacer : $r \sim P^{1/2} a$, or $\rho \sim P^{-1/2}$. Thus, in our limit of large P , the correction is probably not essential.

3.3 COMPLETE PROFILE AND STARBURST LIMIT. — We have integrated numerically the non linear, second order differential equations (11) for $\phi(\rho)$, starting from the parabolic form (14) near the

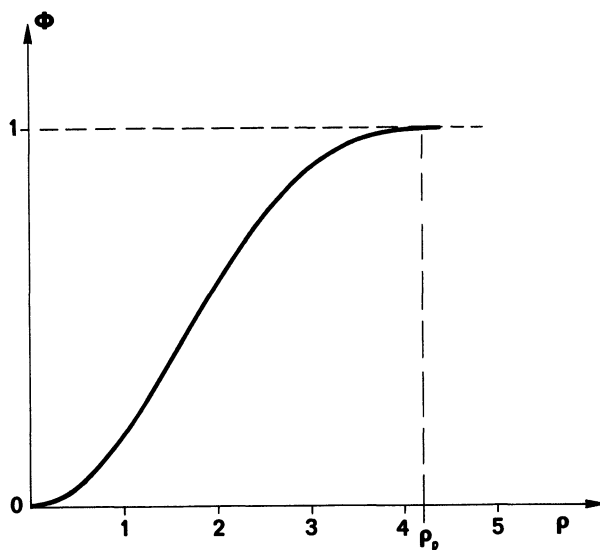


Fig. 3. — Concentration profile in starburst molecules. Notice the parabolic form at small distances ρ , and the stopping point at $\rho = \rho_1 \cong 4.1$. Because of the $-\text{NH}_2$ groups present at the last generation, the physical limiting radius R_1 is somewhat larger than $Pa\rho_1$; see equation (21).

origin. The concentration increases with ρ , and reaches its limiting value $\phi = 1$ at a finite distance (Fig. 3). The limit is ⁽³⁾

$$\rho_1 = 4.1 \pm 0.1. \quad (15)$$

At $\rho > \rho_1$ the starburst process cannot continue : some nitrogen must remain in the form of secondary (or primary) amines. It is of interest to translate the limit ρ_1 in terms of a number of generations m_1 .

Making use of equation (8) we find

$$\begin{aligned} \int_0^{\rho_1} 4 \pi r^2 \phi(r) dr (2 P a^3)^{-1} &= 1 + 3.2^{m_1-1} \cong 3.2^{m_1-1}, \\ &= 2 \pi P^2 \int_0^{\rho_1} \rho^2 \phi(\rho) d\rho. \end{aligned} \quad (16)$$

The result is

$$m_1 = 2.88 \ln P + 4.4 \pm 0.2. \quad (17)$$

3.4 RELATION BETWEEN RADIUS R AND MOLECULAR WEIGHT M . — Let us stop the growth process after a certain number of generations m ($< m_1$). The radius $r(m)$ gives us the position of the last tertiary amines N as shown on figure 2. The polymer radius is related to the position of the NH_2 groups, and is $R \sim r(m + 1)$. The total number of tertiary amines is

$$v = 1 + 3.2^{m-1} = \int_0^{r(m)} 4 \pi r^2 \phi(r) dr (2 P a^3)^{-1}. \quad (18)$$

The central nitrogen carries 3 branches ; all other tertiary amines carry 2 branches. Thus the total molecular weight is

$$\begin{aligned} M &= M_N + 3 P M_0 + [v(m) - 1] (M_N + 2 P M_0), \\ &\cong M_0 \int_0^{r(m)} 4 \pi r^2 \phi(r) dr, \end{aligned} \quad (19)$$

where M_N ($= 14$) is the molecular weight of the cross link, $P M_0$ the molecular weight of one spacer, and we have assumed $P M_0 \gg M_N$. Then

$$\frac{M}{M_0} = P^3 \int_0^{\rho(m)} 4 \pi \rho^2 \phi(\rho) d\rho, \quad (20)$$

while the polymer radius is

$$R = P a \rho(m + 1).$$

⁽³⁾ The mathematical singularity may be located somewhat beyond the value quoted in equation (15) : the accuracy of our integration (based on a pitch $\Delta\rho = 10^{-2}$) is not sufficient to describe the region $\rho > 4$ in detail. But physically the value (15) is indeed the value at which $\phi(\rho)$ saturates.

Going blindly to the continuum limit, we might be tempted to write $\rho(m + 1) \sim \rho(m)$. However, because the elongations are strong near the starburst limit, it is preferable to keep the correction, and to write

$$\begin{aligned} \frac{R}{Pa} &= \rho(m + 1) \cong \rho(m) + \frac{d\rho}{dm} \\ &= \rho(m) + \frac{\ln 2}{\rho^2 \phi(\rho)} \int_0^{\rho(m)} d\rho' \rho'^2 \phi(\rho'), \end{aligned} \quad (21)$$

where we have made use of equation (9). From the numerical solution $\phi(\rho)$ of the self consistent field equations, one can then construct, for a given $\rho(m)$, the corresponding value of $M/P^3 M_0$ via equation (20), and of $R/(Pa)$ via equation (21). The resulting plot of $R(M)$ is shown on figure 4.

a) *In the core region*, where $\phi(\rho) \sim \rho^2$ (Eq. 14) we have

$$\frac{R}{Pa} = \rho(m) [1 + (\ln 2)/5] = 1.14 \rho(m), \quad (22)$$

and

$$\frac{M}{P^3 M_0} = \frac{6 \pi (\ln 2)}{25} \rho^5(m) = 0.523 \rho^5(m). \quad (23)$$

Thus

$$\frac{M}{M_0} = 0.272 \left(\frac{R}{a} \right)^5 P^{-2}, \quad (24)$$

and the radius increases like $M^{0.2}$.

b) *At the starburst limit* ($\rho(m) = \rho_1$) we find a certain molecular weight M_1

$$\frac{M_1}{M_0} = (250 \pm 30) P^3, \quad (25)$$

and a limiting radius R_1 ,

$$\frac{R_1}{Pa} = 4.9 \pm 0.2. \quad (26)$$

Thus, if we consider different starburst limits, with different spacer lengths P , we expect to find for the series

$$\frac{M_1}{M_0} \cong 2.1 \left(\frac{R_1}{a} \right)^3. \quad (27)$$

The uncertainties in all these formulae originate in the uncertainty for the limiting value of ρ_1 (Eq. (15)). This could easily be improved by more precise numerical integration of equations (11) but, in view of the very crude nature of the model, this improvement could not be really meaningful.

4. Discussion.

The main (and rather obvious) conclusion is that the « starburst » type of growth can exist only for a finite number of generations $m \leq m_1$. The limit m_1 is an increasing function of spacer length (Eq. (17)). For molecules below the limit, the predicted relation between molecular weight and

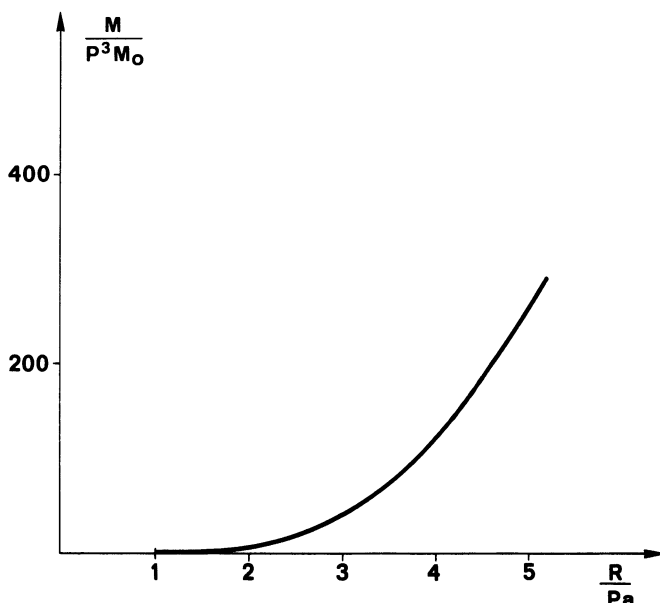


Fig. 4. — Relation between molecular weight M and radius R for starburst molecules with spacers of P monomers and extended length Pa .

size is displayed on figure 4. This plot does not lead to a very clear cut exponent (except in the early stages $M \ll M_1$). Unpublished results by Tomalia *et al.* on the specific viscosity [1] suggest $R(M) \sim M^{0.4}$, while our predictions are $R \sim M^{0.2}$ at low M and $R \sim M^{0.33}$ beyond the starburst limit (the latter corresponding to a growth at constant density).

We expect the starburst structures to be somewhat flexible in the early stages ($m \ll m_1$) but quite rigid (at least in their outer surface) when $m = m_1$. For many chemical applications where a stereospecific surface site is described, it may be preferable to work at $m \sim m_1$.

The present calculation suffers from many defects. In particular, our replacement of the discrete generation index by a continuous variable m is not very good for these strongly elongated structures. The whole scheme becomes meaningful only for rather large values of P (and thus of m_1) which are not desirable in practice. But certain qualitative features concerning the core structure and the starburst limit, are probably meaningful.

Similar calculations could of course be performed for different geometries : e.g. when the initiator is not single, but when we have a strong of initiators equally spaced on a linear polymer (or when we initiate from a flat surface). These calculations will imply the introduction of an extra parameter (the initiator density) and will be more complex : the early stages of growth are still 3 dimensional, but the late stages become 2 dimensional (or one dimensional, depending on the case at hand). In the cross over region the starburst surface shows some interesting cusps, which may become a natural locus for stereochemically active sites.

Our discussion assumed that the reactive functions at each generation were fully saturated. Actually, even with high concentrations of reactants, this need not hold when we reach values of m slightly below m_1 . These situations of partial saturation can be analysed by similar methods, described in the appendix.

Acknowledgments.

This work has been initiated by the recent public presentation of Dr Tomalia's work (Ref. [1]). We want to thank him for a very stimulating discussion.

Appendix : Incomplete reactions.

All the above discussion assumed that, at each step, the amine function $-NH_2$ were completely substituted $NH_2 \rightarrow NR_2$. We shall now briefly discuss the modifications occurring when this is not exactly true : consider one of the hydrogens from the $-NH_2$ function, and call p its probability of having been reacted. In dilute solution we might write

$$\frac{p}{1-p} = kc, \quad (A.1)$$

where c is the concentration of reactant R in solution, and k an equilibrium constant. In our growing molecule, we may assume that k is reduced by steric hindrance

$$k \rightarrow kf(\phi), \quad (A.2)$$

where $f(0) = 1$ and $f(1) = 0$. The complete structure of $f(\phi)$ will depend on stereochemical details, but for many qualitative purposes we might simply assume $f(\phi) = 1 - \phi$. Substituting (A.2) into (A.1) we may write

$$p = \frac{zf(\phi)}{1 + zf(\phi)} \quad (A.3)$$

where $z = kc$ is assumed fixed (and large). Let us now consider simultaneously the two H functions of one $-NH_2$ group, and assume (for simplicity) that they are independent. Then the probability for complete reaction is

$$w_2 = p^2, \quad (A.4)$$

while the probability for a single reaction is

$$w_1 = 2p(1-p). \quad (A.5)$$

The average growth ratio $g(\phi)$ at one generation is thus

$$g(\phi) = 2w_2 + 1w_1 = \frac{2zf(\phi)}{1 + zf(\phi)}. \quad (A.6)$$

We can now use this value in our generation counting, replacing equation (8) by

$$dv = \ln |g(\phi)| v dm \quad (A.7)$$

and equations (11) are then transformed into

$$\phi(\rho) = \rho^{-2} \frac{d}{d\rho} [\rho^2 \phi(\lambda) / \ln [g(\phi)]] . \quad (A.8)$$

The main effect is then to eliminate the singularity of $\phi(\rho)$ at $\rho = \rho_1$. The profile $\phi(\rho)$ becomes continuous and saturates (to $\phi = 1$) only when $\rho \rightarrow \infty$. Thus the existence of a finite reaction level (finite z) gives a certain width to the starburst limit. But for high z the results are practically unchanged.

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