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Star shaped polymers : a model for the conformation and its concentration dependence

M. Daoud and J. P. Cotton

Laboratoire Léon-Brillouin, CEN Saclay, 91191 Gif sur Yvette Cedex, France

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Résumé. — Nous présentons un modèle qui décrit la conformation de polymères branchés en étoile en tenant compte de la variation radiale de la concentration en monomères $\varphi(r)$.

Pour une étoile isolée, lorsque r augmente ($r = 0$ au centre de l'étoile), $\varphi(r)$ est d'abord une constante ($r < f^{1/2} l$) puis varie comme $(r/l)^{-1}$ pour $f^{1/2} l < r < f^{1/2} v^{-1} l$ avant de se comporter comme $(r/l)^{-4/3}$ ($r > f^{1/2} v^{-1} l$); où f est le nombre de branches de l'étoile, N le nombre de monomères par branches, v et l étant respectivement le volume exclu et la longueur associée à un monomère. Dans ces trois domaines il est montré qu'une branche est toujours en extension relativement à la taille qu'elle aurait si elle était isolée.

Lorsque la concentration est supérieure à celle de recouvrement, la conformation d'une étoile est essentiellement définie par deux longueurs : $\chi(c)$ le rayon à l'intérieur duquel les branches des autres étoiles ne peuvent pénétrer ; il définit un domaine où la conformation de l'étoile est analogue à celle d'une étoile isolée. Au-delà de $\chi(c)$, l'interpénétration des branches fait intervenir une longueur d'écran $\xi(c)$ très analogue à celle rencontrée pour des solutions semi-diluées de polymères linéaires.

Dans tous ces domaines la variation de la taille des étoiles est prévue en fonction de N , f , v et c .

Abstract. — We propose a model giving the conformation of a star shaped polymer by taking into account the radial variation of the monomer concentration $\varphi(r)$.

For an isolated star when increasing r (at the centre of the star $r = 0$), the variation of $\varphi(r)$ is first given by a constant value ($r < f^{1/2} l$) then has a $(r/l)^{-1}$ variation (for $f^{1/2} l < r < f^{1/2} v^{-1} l$) and finally a $(r/l)^{-4/3}$ variation (for $r > f^{1/2} v^{-1} l$); where f is the number of branches, N the number of monomers in a branch and v and l are the excluded volume and the length associated to a monomer. For all these cases, it is shown that the size of a branch is always larger than that of a linear polymer made of N monomers.

Beyond the overlapping concentration the star conformation is obtained from two characteristic lengths essentially : $\chi(c)$ a radius inside which the branches of the other stars do not penetrate, this radius defines a domain where the conformation of a star is similar to that of an isolated one. Beyond $\chi(c)$ the interpenetration of branches is characterized by a screening length $\xi(c)$ very similar to that found for semi-dilute solutions of linear polymers.

For all these regimes the variation of the size of a star is predicted as a function of N , f , v and c .

1. Introduction. — Star shaped polymers have received a continuous attention over a long time [1]. Experimental efforts have been made in order to characterize these branched polymers using light scattering [2, 3] or intrinsic viscosity measurements [4]. Most of the theoretical work was done to determine the conformation of a star polymer in its unperturbed state [5-7]. But difficulties appear when the temperature corresponding to this state has to be defined. Thus the Flory temperature [8] θ for which the excluded volume effects between monomers cancel is different from the temperature θ_{A_2} ($< \theta$) for which the second virial coefficient vanishes [9]. Moreover, the conformation of stars in more concentrated solutions —

above the overlap concentration — has not been studied to our knowledge. We attempt here to predict the swelling properties of a star as a function of the quality of the solvent and the monomer concentration c . This problem was studied for linear polymer chains [10, 11] and we will use some of its results. We will see that even the conformation of a single star includes different regimes for the following reasons : let us consider a *uniform* star made of f branches joining at the origin. Each branch has N statistical units of length l . Because all the branches have to join at the centre, the concentration in this region is very high. When one gets away from the centre, the concentration decreases, leading eventually to the

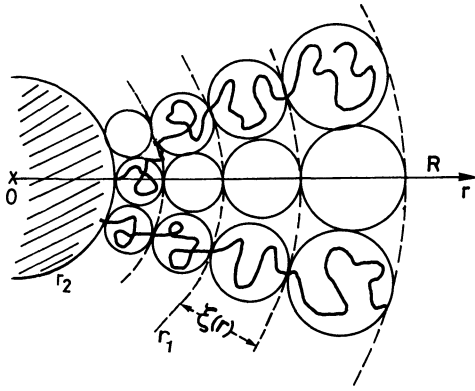


Fig. 1. — A representation of our model : every branch is made of a succession of blobs with a size ξ increasing from the centre of the star to the outside.

single (linear) chain problem in the outside shell where the different branches can be considered as being far apart from each other. Thus, in order to understand the conformation of a star, one has to take into account this variation of the local concentration. This is the aim of the present paper. In order to do this, we will use some results obtained for semi-dilute solutions of linear chains [11]. In the latter case, it was argued that there is locally a single chain behaviour (for more details, the reader is referred to references [10] and [11]). The size ξ of the region where this occurs (blob) depends only on the monomer concentration c , and is the same within the sample. In the present case, if we acknowledge the variation of the local concentration with the distance from the centre of the star, we are led to introduce blobs whose size also depends on this distance. We suppose there is a spherical symmetry around the centre : all the blobs at a given distance from the central point have the same size $\xi(r)$ (see Fig. 1). What this means is that — as for linear chains — we drop the hypothesis of a constant value of the swelling parameter α . Furthermore, we assume that its value depends on the distance to the centre. This will lead us to a decreasing value of $\alpha(r)$ when r decreases, with swollen blobs outside and a deswelling when one goes towards the centre. In fact we will see that the sizes of the blobs can be deduced from one of them by a simple similarity around the central point of the star.

The model and the configuration of a single star will be discussed in section 2, where we evaluate the local swelling of $\xi(r)$, and the radius of a star in different cases depending on the quality of the solvent and the length of a branch. We also discuss briefly the notion of theta temperature in this section. Section 3 extends the model to more concentrated solutions where different stars overlap.

2. The model. — Let us consider a uniform star made of f branches. Every branch has N statistical units of length l . We will use spherical coordinates, the centre of the molecule being at the origin. As we

said above, we expect the local monomer concentration φ to be dependent on the distance r to the centre of the molecule. (Note that $\varphi(r)$ is rather the pair correlation function between the centre of the star and a monomer in a branch.) By analogy to linear molecules [11] we may say that a branch of the star has locally, around a point at a distance r from the centre, a single (free) chain behaviour in a region of size $\xi(r)$ which we call a blob. This size depends on the local concentration $\varphi(r)$. As we expect the latter to increase with decreasing values of r , we are led to the model shown on figure 1 : we define blobs with a size increasing as we go from the centre of the molecule to the outside. In the following we wish to calculate $\varphi(r)$ and $\xi(r)$. In order to do this, we define a *local* swelling parameter $\alpha(r)$ at distance r

$$\alpha(r) \equiv \frac{\xi(r)}{\xi_0(r)} \quad (1)$$

where ξ_0 is the unperturbed size, if the chain were ideal [8, 10]

$$\xi_0(r) \sim n^{1/2}(r) l \quad (2)$$

and $n(r)$ is the number of statistical units in the blob at distance r .

We stress the main difference between this approach and the previous theories : whereas it was usually supposed that there is a uniform swelling of the molecule, we suppose that the blob is much more expanded in the outside than inside : α is also a local parameter that depends on the distance to the centre.

2.1 THE SWOLLEN REGION. — As we said above, inside a blob, every branch behaves as a single chain. Thus in a good solvent and for large distances, we suppose that this local behaviour is swollen. By analogy to the single chain problem [8, 10], we suppose

$$\alpha^5(r) \sim v n^{1/2}(r), \quad (3)$$

where $v = \frac{1}{2} - \chi$ is the monomer excluded volume parameter [8, 10], and χ the usual Flory interaction parameter [8] (not to be confused with the distance $\chi(c)$ to appear later on in section 3). The blob representation provides another relation between α , n and φ . Inside a blob, we have n monomers, so that the dimensionless concentration $\varphi(r)$ is

$$\varphi(r) = \frac{n(r) l^3}{\xi^3(r)} \quad (4)$$

$$\sim n^{-1/2} \alpha^{-3} \quad (5)$$

and, from (2), (3) and (5)

$$\xi \sim n^{3/5} v^{1/5} l \quad (6)$$

$$\alpha^2 \sim v n \varphi. \quad (7)$$

Equations (3) and (6) are the usual Flory results for large values of the swelling parameter α . The difference is that they apply here to the blobs instead of the whole chain as usual. Note also that α , n and ξ in the previous relations depend on r . In order to get this

dependence, we need another equation. A natural hypothesis to make at this level is the following : consider the volume between the spheres of radius r and $r + \xi$. We know that a volume ξ^3 in this shell corresponds to a blob. We are going to suppose that the whole shell contains f blobs. An argument for this hypothesis is that because the inner side is more concentrated than the outer, there is a natural tendency of a branch to « diffuse » towards the outside. The situation here is very similar to what was found for linear polymers grafted on a plane [12, 13]. (The only difference lies in the symmetry which is here spherical.) Thus we have

$$\varphi \sim \frac{nf l^3}{r^2 \xi}. \tag{8}$$

Note that this discussion is also valid for the unswollen case considered below.

Combining (3) to (8) we get

$$n(r) \sim r^{5/3} v^{-1/3} f^{-5/6} l^{-5/3} \tag{9}$$

$$\xi(r) \sim r f^{-1/2} \tag{10}$$

$$\alpha(r) \sim \left(\frac{r}{l}\right)^{1/6} f^{-1/12} v^{1/6} \tag{11}$$

$$\varphi(r) \sim \left(\frac{r}{l}\right)^{-4/3} v^{-1/3} f^{2/3}. \tag{12}$$

Note that equation (10) for the size of the blob is a direct consequence of our hypothesis equation (8) and equation (4) for the local concentration φ .

The results, equations (9) to (12) show that the swelling ratio α is indeed a decreasing function when r decreases and that in the same time the size of the blob decreases.

2.2 THE UNSWOLLEN REGION. — Let us now turn to smaller distances and thus smaller values of α . When the distance to the centre is sufficiently small, α becomes of order unity. Extrapolating the asymptotic behaviour, relation (11), to $\alpha = 1$ we get the cross-over distance r_1 between the swollen regime discussed above and a regime where the blobs are unswollen

$$r_1 \sim f^{1/2} v^{-1} l. \tag{13}$$

For distances smaller than r_1 , the blobs are not swollen anymore. Then we have, instead of (5) and (6)

$$\begin{aligned} \varphi &\sim n^{-1/2} \\ \xi &\sim n^{1/2} l. \end{aligned} \tag{14}$$

Taking (8) into account we find

$$n(r) \sim \left(\frac{r}{l}\right)^2 f^{-1} \tag{9}$$

$$\xi(r) \sim r f^{-1/2} \tag{10}$$

$$\varphi(r) \sim \left(\frac{r}{l}\right)^{-1} f^{1/2}. \tag{12}$$

Several points are noteworthy : first, ξ has the same dependence in both regimes. This is a direct conse-

quence of our assumption equation (8). Second, it is interesting to look at the single chain limit, when f goes to unity. Then $r_1 \sim v^{-1} l$ corresponds to the temperature blob that was introduced for linear chains [14, 15] inside which the chain has an ideal behaviour. For distances larger than r_1 the excluded volume effects are present. In the same way, $\varphi(r)$ goes to the pair correlation function of the linear chain [16]. Finally it is interesting to note that in both the swollen and unswollen regimes, the size of a blob at any distance (larger than r_2 , see below) can be obtained from the size of a reference blob by a simple similarity around the centre of the molecule :

$$\frac{\xi(r)}{\xi(r')} = \frac{r}{r'}.$$

2.3 THE CORE. — When we look at still smaller distances to the centre of the star, we reach a distance r_2 below which the concentration is unity. From (12) we get

$$r_2 \sim f^{1/2} l.$$

Note that for this distance both ξ and n are of order unity. The blob coincides with the statistical unit. This central region which we call the *core* is typical of a star. When f goes to unity, it coincides with the statistical unit. The number of elements on a branch in the core is

$$\begin{aligned} fN_c &\sim \left(\frac{r_2}{l}\right)^3 \\ N_c &\sim f^{1/2}. \end{aligned} \tag{15}$$

Note that if $f \sim N^2$ the core is the whole star. Then the radius is

$$R \sim (Nf)^{1/3} l \sim Nl. \tag{16}$$

Relation (16) is important because it clearly shows that if the number of branches is sufficiently high, the structure of the branches is stretched. This result seems to be natural : when f increases there is less and less space left for the local wriggling of the chains. It is also included in our model where every branch is represented roughly as a linear succession of blobs (see Fig. 1). In the core the blob is just a monomer, and the branch is stretched.

2.4 THE RADIUS. — Thus we find three different regimes for increasing values of the distance r to the centre. The corresponding density profile is shown on figure 2.

- For $r < r_2$, in the core, there is a constant density.
- For $r_2 < r < r_1$ the concentration is high enough to screen out the excluded volume interaction.
- For large distances ($r > r_1$) the excluded volume effects are present within a blob.

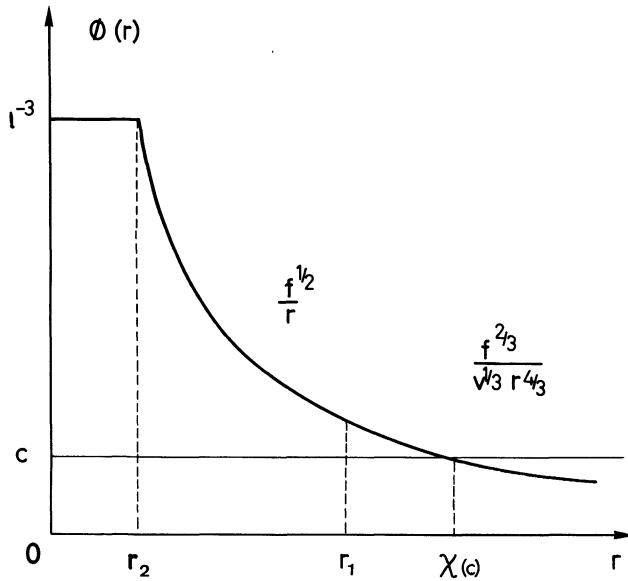


Fig. 2. — The density profile. Three regions appear. In the core ($r < r_2 \sim \sqrt{fl}$) the density is constant. In this region the structure is completely stretched. In the intermediate region ($r_2 < r < r_1 \sim f^{1/2} v^{-1} l$), because the concentration is high the blobs are ideal : $\phi(r) \sim r^{-1} f^{1/2}$. In the outside region the excluded volume effects are present inside the blobs. The length $\chi(c)$ is discussed in section 3.

We can then evaluate the radius of a star by the condition

$$Nfl^3 = \int_0^R \phi(r) dr$$

$$l^3 Nf \sim \int_0^{r_2} r^2 dr + l \int_{r_2}^{r_1} f^{1/2} r dr +$$

$$+ l^{4/3} \int_{r_1}^R r^{2/3} v^{-1/3} f^{2/3} dr \quad (17)$$

giving

$$R \sim \left[Nf + \frac{1}{10} \frac{f^{3/2}}{v^2} + \frac{1}{6} f^{3/2} \right]^{3/5} v^{1/5} f^{-2/5} l \quad (18)$$

and, for very long chains (or high temperatures) we get

$$R \sim N^{3/5} v^{1/5} f^{1/5} l. \quad (19)$$

Equation (19) disagrees with a recent theory by Khokhlov [22].

For shorter branches ($f^{1/2} v^{-2} \gg N \gg f^{1/2}$), even in a good solvent the different branches do not reach the region (2.1) where the excluded volume effects are present. These are screened by the concentration. Then the last term in equation (17) does not contribute anymore. Neglecting the contribution of the core to the radius we find

$$R^2 \sim Nf^{1/2} l^2. \quad (20)$$

Although relation (20) exhibits an « ideal » behaviour because of the molecular weight dependence, the presence of the factor $f^{1/2}$ shows that the radius is in fact larger than it would be for a single linear chain : the branch is more stretched than an ideal chain. This will be discussed in section 2.5.

Finally, for short enough branches ($N < l^{1/2}$) the star reduces to the core which has been discussed above.

2.5 DISCUSSION AND COMPARISON WITH EXPERIMENTAL RESULTS. — Our central results, equations (19) and (20) (see table I), clearly show that the radius of a star is much smaller than the radius of a linear chain with the same molecular weight. This qualitative result is consistent with experimental measurements [2, 17]. In order to have a more precise confirmation of the model, we calculate the ratio g of the radius of a star by the radius R_1 of the equivalent linear chain. From equation (19) we get

$$g = \left(\frac{R}{R_1} \right)^2 \sim f^{-4/5}$$

in a good solvent, for long branches. g is thus a decreasing function which can be measured quite easily when the branches are sufficiently long ($N \gg f^{1/2} v^{-2}$).

Table I. — Dependence of the radius R as a function of the number f of rays, the number N of monomers per ray and the excluded volume v of a monomer.

Regime	R
$N \gg f^{1/2} v^{-2}$	$N^{3/5} v^{1/5} f^{1/5} l$
$f^{1/2} v^{-2} \gg N \gg f^{1/2}$	$N^{1/2} f^{1/4} l$
$f^{1/2} \gg N$	$(Nf)^{1/3} l$

This prediction is compared to the measured values of radius of gyration obtained [2] for star shaped polymers with polystyrene branches. Table II shows

Table II. — Variation of $gf^{4/5}$ for star shaped polystyrene. R is the radius of gyration of stars, R_1 is that of linear polymer with molecular weight fM_w . The data are obtained from reference [2].

M_w branch	f	R (Å)	R_1 (Å)	$gf^{4/5}$
—	—	—	—	—
570 000	8.7	858	1 048	2.10
190 000	10.7	475	824	2.21
—	12.1	484	885	1.99
—	13.4	492	942	2.18
—	14.4	503	986	2.20
—	15.5	503	1 028	2.14
—	12.3	489	897	2.21
110 000	7	328	460	2.41
—	8.2	338	507	2.39
—	9.6	325	558	2.07
—	13	347	666	2.11

a constant value of $gf^{4/5}$ (within an accuracy of 10 %) which confirms the predictions of the relation given just above.

On the other hand, the radius of a star is much larger than that of a single chain of N monomers isolated in the solvent. This is true even for a shorter branch, or a theta solvent⁽¹⁾. We can see this more clearly if we consider the case $R \sim r_1$. This corresponds to a sufficiently high functionality of the central point or to a small excluded volume parameter ($r_1 \sim f^{1/2} v^{-1}$)

$$r \sim r_1 \sim f^{1/2} v^{-1} l. \quad (21)$$

Then (17) reads, always neglecting the contribution from the core

$$l^3 N f \sim \int_0^{r_1} \varphi(r) r^2 dr \sim f^{3/2} v^{-2} l^3 \quad (22)$$

$$N \sim f^{1/2} v^{-2}.$$

Eliminating f or v between (21) and (22) gives

$$R \sim N^{1/2} f^{1/4} l \sim N v l. \quad (23)$$

Thus although we are in a regime where the chain seems to be ideal, cf. relation (20), the structure is actually stretched. Note however that the radius (23) is much smaller than the completely elongated chain length $L = Nl$, as shown by the factor $v (\ll 1)$ in (23). This result is not surprising: our model considers every branch to be made of a linear succession of blobs, even at the theta temperature. This naturally brings us to the discussion of the temperature effects. Let us suppose that the excluded volume parameter is proportional to the temperature difference $v \sim \frac{T - \theta}{\theta}$.

Let us then consider a long star molecule in a good solvent and decrease v , or T . Relation (13) shows that the border-line of the region where the blobs are ideal increases

$$r_1 \sim f^{1/2} v^{-1} l. \quad (13)$$

There is a value v_c for which all the blobs are gaussian. From what we have seen above,

$$v_c \sim N^{-1/2} f^{1/4}. \quad (24)$$

The corresponding temperature is higher than the one for which a single linear chain crosses over to the theta behaviour [18, 19]. However, it is very important to realize that although the blobs are ideal, the branch itself is stretched [see (23)]. Thus the conformation of the chain at the theta temperature is very different from that of a gaussian chain. Let us call g_θ the ratio of the radius of the star at $T = \theta$ by the radius $R_{1\theta}$ of the equivalent linear gaussian chain

$$g_\theta = \left(\frac{R_\theta}{R_{1\theta}} \right)^2 \sim f^{-1/2}. \quad (25)$$

Table III. — Variation of $g_\theta f^{1/2}$ for star shaped polyisoprene. The experimental values of g_θ are obtained from reference [3].

f	g_θ	$g_\theta f^{1/2}$
4	0.65	1.30
6	0.46	1.13
8	0.415	1.17
12	0.33	1.14

This prediction can be tested with the careful experimental results obtained [3] with star shaped polymers of polyisoprene with $f = 4, 6, 8,$ and 12 . The value for $g_\theta f^{1/2}$ as function of f are given in table III showing that equation (25) is rather well verified [23]. For $f = 4$ the experimental value of $g_\theta f^{1/2}$ is greater than the other ones. This discrepancy might possibly originate from the fact that g_θ is obtained from viscosity measurements and hydrodynamic effects are probably not negligible for low f values.

Concerning the temperature effects let us insist on the fact that at the theta temperature, the conformation of a branch has nothing to do with a gaussian chain. In other terms it is misleading to use unperturbed dimensions of the branches in order to predict the theta dimension of a star shaped polymer. This has already been suggested previously [9, 20].

Because of the presence of the core, the temperature at which a branch reaches its unperturbed dimensions can be obtained only for temperatures below θ , when the interaction between monomers of the branches becomes attractive ($v < 0$). Then the blobs start collapsing and the size of the branched polymer can reach a dimension comparable with that of an isolated branch in a theta solvent. This is not of great interest (in our opinion) because it hides the structure of the star. Thus we will not discuss the « theta temperature » any longer and conclude that at the theta temperature the radius of the star is larger than its unperturbed value, in agreement with previous theoretical and experimental work [9, 17, 20, 21] and turn now to the concentration effects.

3. The concentration effects. — In the previous section, we have considered the properties of a single star shaped polymer, i.e. very dilute solutions. When we increase the monomer concentration c , we expect these properties to hold basically, except for correction terms, as long as the stars are far apart from each other. So we expect a cross-over to occur for the different properties around the overlap concentration c^*

$$c^* \sim \frac{Nf}{R^3}$$

where the branches of different stars start overlapping. In the following, we will consider the properties of solutions of stars with concentration within the semi-dilute range, $l^{-3} \gg c \gg c^*$. Let us note that we find different expressions for c^* depending on the length

(1) By theta solvent we mean that of a linear chain. Thus a star made of polystyrene is swollen in cyclohexane for instance.

of every branch. Using the asymptotic expressions we found in last section for the radius of a star, we get

$$c^* \sim N^{-4/5} f^{2/5} v^{-3/5} l^{-3} \quad (N \gg f^{1/2} v^{-2}) \quad (26a)$$

$$c_\theta^* \sim N^{-1/2} f^{1/4} l^{-3} \quad (f^{1/2} \ll N \ll f^{1/2} v^{-2}) \quad (26b)$$

$$c^* \sim l^{-3} \quad N < f^{1/2}. \quad (26c)$$

Note that (26c) corresponds to the case when the stars reduce to their central core, thus never allowing any overlap.

In the other two cases (26a and b), there is an overlap of the branches of different stars. As a result, one might imagine the solution in the following way : around the centre of a star there is a region of space with size χ where the star has a single star behaviour. For distances larger than χ , because of the overlap of the different stars, there is a screening of the interaction and the size of the blob is controlled by the (average) concentration c . This concentration blob just corresponds to the size of the « star blobs » we considered in the previous section, for a distance χ . In other terms we may say that the blobs are controlled by the « star effect » for distances below χ and by the concentration (so that their size is constant) for distances larger than χ .

In order to determine χ and $\xi(c)$, we have to compare the monomer concentration c to the local concentration $\varphi(r)$ around the centre of a star (see Fig. 2).

3.1 GOOD SOLVENTS. — Let us first consider the case when the length of the branches is sufficiently long or when the temperature is high enough ($N > f^{1/2} v^{-2}$). Then the condition for the equality of the local and average concentrations reads

$$l^3 c \sim \left(\frac{\chi}{l}\right)^{-4/3} f^{2/3} v^{-1/3}$$

leading to

$$\chi \sim (l^3 c)^{-3/4} v^{-1/4} f^{1/2} l. \quad (27)$$

So starting from the centre of a star, we find that for distances smaller than χ there is a single star behaviour. For distances larger than χ , because of the overlapping of the different branches, the concentration effects dominate. We can then define a concentration blob with size $\xi(c)$ equal to that of a star blob for $r \sim \chi$. From (10) and (27) we get

$$\xi(c) \sim (cl^3)^{-3/4} v^{-1/4} l. \quad (28)$$

Note that we find the same law as for a solution of linear chains with same concentration [11]. There is however a basic difference between the linear chains and the stars : in the latter case, there is an extra length χ . Around the centre of every star, there is a region with size χ where the star has a single star behaviour. For distances larger than χ , there is an overlap of the branches and the solution looks like a

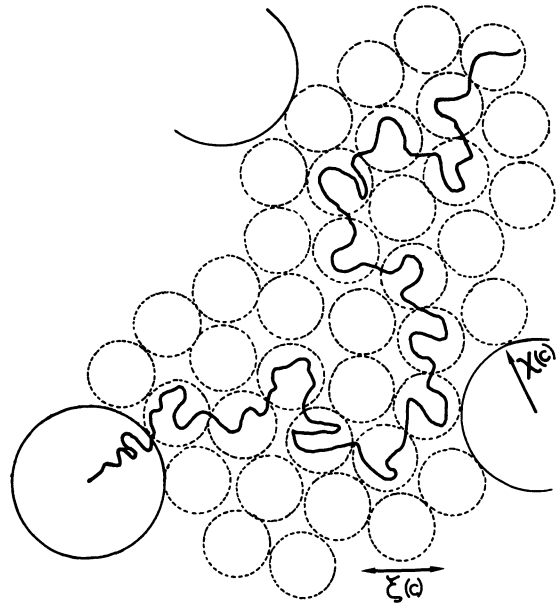


Fig. 3. — Representation of a branch of a star shaped polymer in the semi-dilute regime.

solution of linear chains. The corresponding representation of this model is shown on figure 3.

3.2 THETA SOLVENT. — The situation described in the preceding section may happen as long as χ is larger than r_1 (see Eq. (13) and below). For shorter branches or lower temperatures ($f^{1/2} \ll N \ll f^{1/2} v^{-2}$) we have seen in section 2.2 that the star blobs are not swollen any more. Using then (13') instead of (13) for the local concentration, we find

$$\chi \sim (cl^3)^{-1} f^{1/2} l \quad (27')$$

leading to a concentration blob size

$$\xi(c) \sim (cl^3)^{-1} l. \quad (28')$$

Note that these results also hold when the concentration c is large enough. The cross-over concentration c^{**} between the two regimes is obtained by comparing (27) to (27') :

$$c^{**} l^3 \sim v. \quad (29)$$

Here again, we find that this cross-over concentration is the same as the one between good and theta solvents for semi-dilute solutions of linear chains [19]. As long as we are interested in properties far from the centre of the stars, the two cases are very comparable.

3.3 THE MELT. — Finally, when the concentration goes to unity, the region where the stars do not overlap reduces to the core

$$\chi \sim f^{1/2} l \quad (30)$$

while the size of the blob goes to the step length.

At this point, a subtle distinction has to be made between stars with long or short branches : in all the

preceding (Eq. (27) and below) we have explicitly supposed that the monomer concentration far from the centres of the star is c . This is valid as long as the branches are very long ($N \gg f^{1/2}$) so that the concentration increases around the centre of a star can be considered as a fluctuation. When the branches are not very long, this becomes more and more approximate because a non negligible fraction of the monomers is located in the central part with size χ . One would then have to define an effective concentration \bar{c} in the overlapping regions, lower than the total monomer concentration. This will not be done here.

3.4 RADIUS. — Let us now turn to the radius of the star, which is the same as that of a branch. We have seen above that for concentrations above c^* , our model consists in two successive regions around the centre of a star : a first region with size χ where the behaviour is the same as for a single star, followed by a region where the concentration effects dominate and where we have blobs with a constant size $\xi(c)$, so that we expect a behaviour identical to that of linear chains in the latter region. Because of this structure, we do not expect scaling to hold. Instead, we are going to suppose that the total radius of the star is just the sum of the two contributions discussed above.

$$R \sim \chi + R_b, \quad (31)$$

where R_b is the radius of the outer part of a branch, made of blobs with equal size $\xi(c)$. This part can be considered as a linear chain made of $(N - n)$ elements, where n is the number of units in χ . Then, the radius of this part is [10, 11]

$$R_b^2 \sim (N - n) (cl^3)^{-1/4} v^{1/4} l^2 \quad (32)$$

and is independent of f .

The number of elements n in the region with size χ where the behaviour is the same as for a single star can be obtained for instance by applying relation (19) for the radius : if we suppose this part to be large, i.e. the concentration not to be too high

$$\chi \sim n^{3/5} f^{1/5} v^{1/5} l$$

we find

$$n \sim (cl^3)^{-5/4} v^{-3/4} f^{1/2} \quad (33)$$

leading to

$$\frac{R}{l} \sim (cl^3)^{-3/4} v^{-1/4} f^{1/2} + [N - (cl^3)^{-5/4} v^{-3/4} f^{1/2}]^{1/2} (cl^3)^{-1/8} v^{1/8} \quad (34)$$

for a star in a good solvent and in the semi-dilute regime.

Relation (34) allows us to define two different regimes depending on the relative value of the two terms : for lower concentrations the first term, χ , dominates the second, while the latter is more important for higher concentrations. Comparing these two

terms, we are led to introduce a cross-over concentration c , between the two regimes

$$c_1 \approx N^{-4/5} v^{-3/5} f^{4/5} l^{-3} \sim c^* f^{2/5} \quad (35)$$

and we have

$$R \approx \chi \sim (cl^3)^{-3/4} v^{-1/4} f^{1/2} l \quad \text{for } c^* < c < c_1 \quad (36a)$$

$$R \approx N^{1/2} (cl^3)^{-1/8} v^{1/8} l \quad \text{for } c \gg c_1. \quad (36b)$$

Note however that except for high values of the branching f , c_1 and c^* are close to each other so that it might be difficult to observe (36a) experimentally because of the narrowness of the region where it is valid.

For lower temperatures or shorter branches ($Nfv^2 < 1$), there is no swelling of the blobs, neither in the star like region, χ , nor for the concentration blobs. Using then (27') instead of (27) we get

$$\frac{R}{l} \sim (cl^3)^{-1} f^{1/2} + [N - (cl^3)^{-2} f^{1/2}]^{1/2} \quad (34')$$

for a star at temperatures around theta and in the semi-dilute regime.

Here again, we can define a concentration c_1^0 above, which separates a regime in which the first term in the right hand side of (34') is dominant from a higher concentration regime in which the second term is important

$$c_1^0 \approx (Nf^{-1})^{-1/2} l^{-3} \sim c_0^* f^{1/4}.$$

Finally, if we vary the temperature, or the excluded volume parameter, $v \sim \frac{T - \theta}{\theta}$, comparison of equations (34) and (34') shows that we cross over from the good solvent to the « theta » solvent behaviour when

$$c \sim vl^3.$$

Finally, in the melt the structure is made of the cores immersed in large regions where the different branches overlap strongly and behave like linear chains

$$\frac{R}{l} \sim f^{1/2} + N^{1/2}.$$

Note that when the branches become shorter, the core becomes more important and the overlap of different star decreases.

4. Conclusion. — We have studied the behaviour of a star shaped polymers in dilute and semi-dilute solutions. For a single star, our model defines a blob with size $\xi(r)$ increasing as we go from the centre of the star to the outside. The basic hypothesis is that in the region between the spheres with radius r and $r + \xi$

there are only f blobs. This is a generalization of what is assumed for chains grafted on a plane [12, 13]. When the molecular weight of a branch is high, and in a good solvent we find a radius $R \sim N^{3/5} f^{1/5} l$. This result might be compared with the result of a crude Flory type theory : We have two contributions to the free energy :

— an elastic term

$$F_{el} \simeq f \frac{R^2}{R_0^2} \sim f \frac{R^2}{Nl^2}$$

where we supposed that the elastic constant of a branch is related to the *unperturbed* dimensions,

— an interaction term evaluated by considering that we have Nf interacting elements in a volume R^d

$$F_{int} \simeq v(Nf)^2/R^d.$$

Minimizing the free energy leads to

$$R \sim N^{3/5} v^{1/5} f^{1/5} l \quad (d = 3) \quad (37)$$

in agreement with what was found above in a good solvent, equation (19), but in disagreement with (20) for a theta solvent.

In fact, a careful examination of the results of last section leads us to draw some analogy between a star with f branches made of N elements each and a linear chain made of $Nf^{1/2}$ elements interacting with an excluded volume parameter $vf^{-1/2}$. Then, if we adopt this analogy, the two contributions to the free energy are

$$F_{el} \sim T \frac{R^2}{Nf^{1/2} l^2}$$

$$F_{int} \sim (Nf^{1/2})^2 \frac{vf^{-1/2}}{R^d}$$

leading of the results quoted in section 2 (relations (19) and (20)). However this analogy may also be misleading because of the same reasons as discussed above : The stretched structure is hidden, as are the complications arising around the theta temperature. Also, we do not really expect any scaling relation to hold, as would be the case if there were a deep analogy between the two problems.

For higher concentrations, $c > c^*$, the branches of different stars overlap. We are then led to define two different regions when the distance r to the centre of a star is varied :

— For small distances, $r < \chi$, the behaviour is the same as for a single star.

— For larger distances, the behaviour is the same as for linear chains. The size of the blobs is independent of f and depends only on the monomer concentration.

The radius of the star, which is taken equal to that of a branch has a contribution from these two regions (see Eqs. (34) and (34')). Note that when the size of the branches decreases, so does the amount of overlap. When $f \sim N^2$ there is no overlap, and we have a solution of hard spheres. Every branch then is completely stretched.

These predictions can be tested by light or neutron scattering experiments using stars with one branch labelled.

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