

## Short Communication

**Static Properties of a Star Polymer in a High Molecular Weight Solvent**

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**Abstract.** — Recently, Raphaël, Pincus and Fredrickson considered the static properties of an isolated star polymer ( $f$  arms,  $N$  monomers per arm) dissolved in a melt of linear chains of degree of polymerization  $P < N$ , which are chemically identical to the star arms (*Macromolecules* **26** (1993) 1996). In the present article we show that the results obtained by these authors are valid only for stars with a high enough number of arms  $f > P^{1/2}$ . For  $f < P^{1/2}$ , a new Gaussian region appears within the star structure. We predict that the  $N$ -monomer volume fraction varies as  $\phi(r) \cong 1$  (dense region) for  $r < af$ ,  $\phi(r) \cong f(r/a)^{-1}$  for  $af < r < aPf^{-1}$  and  $\phi(r) \cong P^{1/3}f^{2/3}(r/a)^{-4/3}$  for  $r > aPf^{-1}$ . Our study is restricted to scaling laws; the exact prefactors in our formulae remain undetermined.

**Introduction**

In the last twenty years, there has been an increased interest in *star polymers*, a special class of branched polymers in which one end of each linear chain is tethered to a small central core to form a single molecule [1]. A particularly simple model for the static properties of an isolated star polymer ( $f$  arms,  $N$  monomers per arm) in a solvent of low molecular weight was proposed by Daoud and Cotton 13 years ago [2]. This scaling picture was generalized by Raphaël *et al.* [3] to the case of a star polymer dissolved in a melt of linear chains of degree of polymerization  $P < N$ , which are chemically identical to the star arms. According to these authors, the  $N$ -monomer volume fraction,  $\phi$ , varies with the distance from the center of the star,  $r$ , as

$$\phi(r) \cong 1 \quad r < af^{1/2}P^{1/4} \quad (1a)$$

$$\phi(r) \cong P^{1/3}f^{2/3}(a/r)^{4/3} \quad af^{1/2}P^{1/4} < r < R \quad (1b)$$

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where  $a$  is the monomer size. The radius of the star,  $R$ , can be deduced from the condition  $Nfa^3 = \int_0^R d^3r\phi(r)$ . Using equations (1a) and (1b) one obtains [3,4]:

$$R \cong aN^{3/5}f^{1/5}P^{-1/5} \quad N > f^{1/2}P^{3/4} \quad (2a)$$

$$R \cong aN^{1/3}f^{1/3} \quad N < f^{1/2}P^{3/4} \quad (2b)$$

One should realize, however, that the results (1) and (2) cannot be valid for too small values of  $f$ . Indeed, in the limit of a linear molecule (i.e., for  $f = 1$ ), these results do not extrapolate to the well known results [5]:  $R \cong aN^{3/5}P^{-1/5}$  for  $P < N^{1/2}$ , and  $R \cong aN^{1/2}$  for  $P > N^{1/2}$ . It will be shown below that the results (1) and (2) are valid only for stars with a high enough number of arms  $f > P^{1/2}$ . In the present paper, we will therefore focus our attention on the reverse case ( $f < P^{1/2}$ ).

### Scaling Analysis

Consider a star polymer made of  $f$  identical arms, each arm consisting of  $N$  monomers of size  $a$ . The star polymer is immersed in a melt of linear chains of degree of polymerization  $P$ , chemically identical to the star arms. We assume that  $f < P^{1/2}$ . Let us first consider what happens far away from the center. Following the idea of Daoud and Cotton [2], we describe each arm as a succession of growing spherical blobs. At a given distance  $r$  from the center, there are  $f$  blobs, one for each polymer chain. Since  $f$  blobs cover a sphere of radius  $r$ , the blob radius is given by

$$\xi(r) \cong rf^{-1/2} \quad (3)$$

Within one blob, the arm behaves as an isolated chain and the number of monomers per blob,  $g(r)$ , is given by  $\xi(r) \cong ag(r)^{3/5}P^{-1/5}$ . The  $N$ -monomer volume fraction is given by

$$\phi(r) \cong a^3g(r)\xi(r)^{-3} \cong P^{1/3}f^{2/3}(r/a)^{-4/3} \quad (4)$$

Equations (3) and (4) are valid as long as the blob size  $\xi$  is larger than the size of a melt blob,  $l_c$  [5]. Consequently, these equations are valid only in the outer part of the star. This region, called S2, is defined by the condition  $r > aPf^{1/2}$ .

For  $r < aPf^{1/2}$ , blobs from different chains overlap laterally (see Fig. 2) and their size  $\Lambda$  is intermediate between  $rf^{-1/2}$  and  $l_c$  [6]. At a scale smaller than  $\Lambda$ , the arm behaves like an ideal chain of  $g_\Lambda \cong (\Lambda/a)^2$  monomers. In order to calculate the subunit size  $\Lambda$ , we have to consider the perturbation parameter  $\zeta \cong \frac{g_\Lambda(r)}{P}\phi(r)$  where  $\phi(r) \cong a^3\frac{g_\Lambda(r)}{\Lambda(r)(rf^{-1/2})^2}$  is the  $N$ -monomer volume fraction [6]. At a scale larger than  $\Lambda$ , the arm ceases to be ideal: the subunit size  $\Lambda$  is therefore determined by the condition  $\zeta \cong 1$ . This leads to  $g_\Lambda(r) = P^{2/3}f^{-2/3}(r/a)^{4/3}$  and

$$\Lambda(r) = aP^{1/3}f^{-1/3}(r/a)^{2/3} \quad (5)$$

One can easily show that in this region, called S1 (see Fig. 1), the  $N$ -monomer volume fraction is still given by equation (4), although the structure of the blobs has changed.

When  $\Lambda(r)$  becomes comparable to  $r$ , the  $f$  blobs (corresponding to the  $f$  arms of the star) overlap completely. This occurs for  $r \cong aPf^{-1}$ . For  $r \leq aPf^{-1}$ , the  $N$ -monomer volume fraction is thus simply given by  $f$  times the volume fraction of a Gaussian chain:

$$\phi(r) \cong f\frac{a}{r} \quad (6)$$

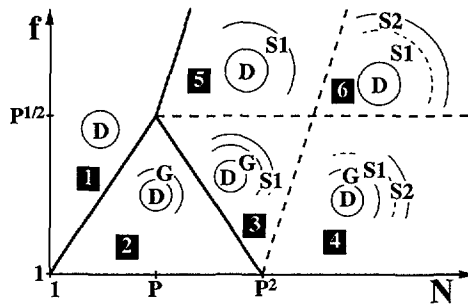


Fig. 1. — Various regimes for a star polymer ( $f$  arms,  $N$  monomers per arm) dissolved in a melt of linear chains of degree of polymerization  $P$ , which are chemically identical to the star arms. The cross over between the different regions are given by:  $1/2, N \cong f^2$ ;  $2/3, N \cong P^2 f^{-2}$ ;  $3/4, N \cong P^2 f^{1/2}$ . The upper part of the figure corresponds to the case  $f > P^{1/2}$  studied in reference [3]; the cross over between the different regions are given by:  $1/5, N \cong P^{3/4} f^{1/2}$ ;  $5/6, N \cong P^2 f^{1/2}$

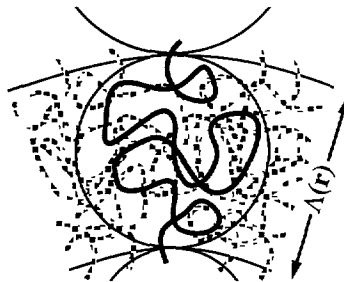


Fig. 2. — Schematic representation of the local structure of the star polymer in the region S1 ( $aPf^{-1} < r < aPf^{1/2}$ ). Each arm can be pictured as a succession of growing spherical blobs of size  $\Lambda$  (intermediate between  $rf^{-1/2}$  and  $l_c$ ). Note that blobs from different chains overlap laterally.

For even smaller values of  $r$ , we reach a distance below which the  $N$ -monomer volume fraction is unity ( $\phi \cong 1$ ). Using equation (6), we find that the radius of this dense region (called region D) is given by  $af$ . To summarize, a star with long arms ( $N > P^2 f^{1/2}$ ) consists of four regions delimited by the radii  $af, aPf^{-1}$  and  $aPf^{1/2}$

The radius of the star,  $R$ , may be obtained from the integral condition [7]

$$Nfa^3 = \int_0^R d^3r \phi(r) \tag{7}$$

Using equations (4) and (6) one obtains (Fig. 3)

$$R \cong aN^{3/5} f^{1/5} P^{-1/5} \quad N > P^2 f^{-2} \tag{8}$$

$$R \cong aN^{1/2} \quad f^2 < N < P^2 f^{-2} \tag{9}$$

$$R \cong aN^{1/3} f^{1/3} \quad N < f^2 \tag{10}$$

The free energy of a star with  $N > f^2$  can be written as the sum of two contributions due to the inner, dense region (the “core”,  $r < af$ ) and the remaining part of the star (the “corona”,  $af < r < R$ ):  $F_{\text{star}} = F_{\text{core}} + F_{\text{corona}}$ . The free energy of the corona is given by the  $kT$  per

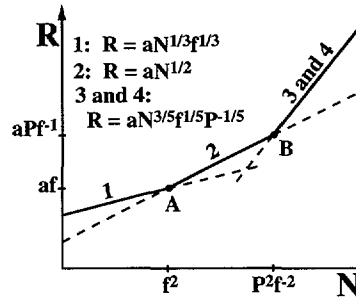


Fig. 3. — Variations of the star radius,  $R$ , as a function of the arm length,  $N$ . Note that for  $N < f^2$ , the star radius  $aN^{1/3} f^{1/3}$  is greater than  $aN^{1/2}$  (the arms are stretched with regard to their natural size). Numbers 1-4 refer to the corresponding regimes of Figure 1.

blob Ansatz

$$\frac{F_{\text{corona}}}{kT} \cong f + \int_{af}^{aPf^{1/2}} \frac{4\pi r^2 dr}{\Lambda(r)(rf^{-1/2})^2} + \int_{aPf^{1/2}}^R \frac{4\pi r^2 dr}{(rf^{-1/2})^3} \tag{11}$$

where in the second term of the r.h.s the quantity  $\Lambda(r)$  is given by equation (5). The first term corresponds to the free energy of the ideal parts of the arms (spatial region  $af < r < aPf^{-1}$ ) Hence

$$\frac{F_{\text{corona}}}{kT} = f \quad f^2 < N < P^2 f^{-2} \tag{12}$$

$$\frac{F_{\text{corona}}}{kT} = N^{1/5} f^{7/5} P^{-2/5} \quad P^2 f^{-2} < N < P^2 f^{1/2} \tag{13}$$

$$\frac{F_{\text{corona}}}{kT} = f^{3/2} \{1 + \ln(R/(aPf^{1/2}))\} \quad N > P^2 f^{1/2} \tag{14}$$

The contribution  $F_{\text{core}}$  accounts for the stretching penalty in the inner, dense region. A crude evaluation of  $F_{\text{core}}$  may be obtained by assuming that for each arm the part of the chain inside the core ( $f^2$  monomers) is stretched to an end-to-end distance of the order of the core radius

$$\frac{F_{\text{core}}}{kT} \cong f \frac{(a(f^2)^{1/3} f^{1/3})^2}{a^2(f^2)} \cong f \quad N > f^2 \tag{15}$$

Note that for a star with  $N < f^2$ , the corona is absent and the core free energy is given by

$$\frac{F_{\text{core}}}{kT} \cong f \frac{(aN^{1/3} f^{1/3})^2}{a^2 N} \cong f^{5/3} N^{-1/3} \quad N < f^2 \tag{16}$$

### Concluding Remarks

(i) In this article, we have considered the static behavior of a star polymer ( $f$  arms,  $N$  monomers per arm) immersed in a melt of linear chains ( $P$  monomers per chain) chemically identical to the star arms, assuming  $f < P^{1/2}$ . Our main result is the appearance of a Gaussian region within the star structure [8]. In particular, for  $P^2 f^{-2} < N < P^2 f^{1/2}$ , the star radius is given by  $R \cong aN^{1/2}$ . The origin of this result can be understood rather simply: since the star arms are immersed in a melt of chemically identical chains, they cannot be confined to a size smaller than their natural size  $aN^{1/2}$ . Since both the “dense star radius” ( $aN^{1/3} f^{1/3}$ ) and the “swollen

star radius" ( $aN^{3/5}f^{1/5}P^{-1/5}$ ) would be smaller than  $aN^{1/2}$  for  $f^2 < N < P^2f^{-2}$  (see Fig. 3), the star radius is given by  $aN^{1/2}$  in this regime.

(ii) For  $N < f^2$ , the  $N$ -monomer volume fraction inside the star is of order unity: the star is dense. It is important to realize, however, that the star radius  $aN^{1/3}f^{1/3}$  is greater than  $aN^{1/2}$ : Due to steric hindrance (all the arms originate from the same point), the arms are stretched with respect to their natural size.

(iii) In the limit of a star with very few arms ( $f \rightarrow 1$ ), the results (8)-(10) extrapolate to the usual linear chain regimes: the chain is Gaussian ( $R = aN^{1/2}$ ) if  $P > N^{1/2}$  and it is swollen ( $R = aN^{3/5}P^{-1/5}$ ) if  $P < N^{1/2}$  (for  $f = 1$ , the dense region is reduced to the size of a monomer)

(iv) For ( $f = P^{1/2}$ ), points A and B of Figure 3 coincide and the Gaussian region disappears. For  $f > P^{1/2}$ , one recovers all the results of reference [3].

(v) In this article we have considered the static properties of a single star polymer. Concentration effects will be published separately.

### Acknowledgments

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### References

- [1] Grest G.S., Fetters L.J., Huang J.S. and Richter D., *Adv. Chem. Phys.*, Vol. **94**, E. Prigogine and S. A. Rice Eds. (New York, 1996).
- [2] Daoud M., Cotton J.-P., *J. Phys. France* **43** (1982) 531.
- [3] Raphaël E., Pincus P. and Fredrickson G.H., *Macromolecules* **26** (1993) 1996-2006.
- [4] The results (1) and (2) are easily generalized to the case  $P > N$ ; see the upper part of Figure 1.
- [5] Consider an isolated linear chain, with degree of polymerization  $N$ , dissolved in a melt of shorter, chemically identical chains with degree of polymerization  $P$ . The chain behaves like a string of subunits, usually called *melt blobs*, each containing  $g_c = P^2$  monomers. Within one melt blob the behavior is ideal, leading to a blob size  $l_c = aP$ . Different melt blobs repel each other, and the resulting self-avoiding chain (of unit step  $l_c$ ) has a size  $R \cong (N/g_c)^\nu l_c$  where  $\nu = 3/5$  is the Flory 3-dimensional exponent. See, e.g., de Gennes P.-G., "Scaling Concepts in Polymer Physics" (Cornell University Press, Ithaca, Fourth Printing, 1985).
- [6] Aubouy M., Fredrickson G.H., Pincus P., Raphaël E., *Macromolecules* **28** (1995) 2979-2981.
- [7] Note that the results concerning the star radius  $R$  may be recovered by minimizing the Flory free energy per arm  $\frac{F_{\text{arm}}}{kT} \cong \frac{R^2}{Na^2} + N\frac{a^3}{P}c + N\frac{a^6}{P}c^2$  (where  $c \cong Nf/R^3$  is the average monomer concentration of the star), keeping in mind the conditions  $a^3c \leq 1$  (i.e.  $Nfa^3 \leq R^3$ ) and  $R \geq aN^{1/2}$
- [8] A somewhat similar Gaussian behavior was described by Birshtein and Zhulina for stars with a small number of semiflexible branches in low molecular weight solvents. See Birshtein T.M., Zhulina E.B., *Polymer* **25** (1984) 1453-1461.