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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, ϕ , 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

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

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

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

Equations (3) and (4) are valid as long as the blob size ξ 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 $r > a P f^{1/2}$.

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

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

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 $r \cong a P f^{-1}$. For $r \leq a P f^{-1}$, the N -monomer volume fraction is thus simply given by f times the volume fraction of a Gaussian chain:

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

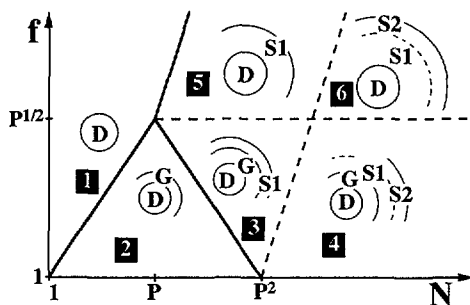


Fig. 1. — Various regimes for a star polymer (f arms, N monomers per arm) dissolved in a melt of linear chains of degree of polymerization P , which are chemically identical to the star arms. The cross over between the different regions are given by: 1/2, $N \cong f^2$; 2/3, $N \cong P^2 f^{-2}$; 3/4,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

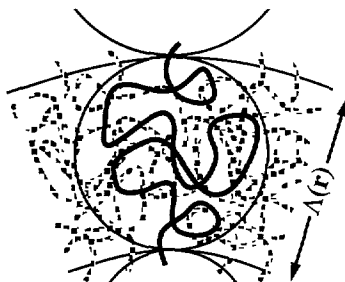


Fig. 2. — Schematic representation of the local structure of the star polymer in the region S1 ($aPf^{-1} < r < aPf^{1/2}$). Each arm can be pictured as a succession of growing spherical blobs of size Λ (intermediate between $rf^{-1/2}$ and l_c). Note that blobs from different chains overlap laterally.

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]

$$Nfa^3 = \int_0^R d^3r \phi(r) \quad (7)$$

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

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

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

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

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

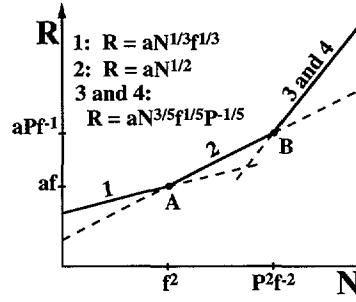


Fig. 3. — Variations of the star radius, R , as a function of the arm length, N . Note that for $N < f^2$, the star radius $aN^{1/3}f^{1/3}$ is greater than $aN^{1/2}$ (the arms are stretched with regard to their natural size). Numbers 1-4 refer to the corresponding regimes of Figure 1.

blob Ansatz

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

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

$$F_{\text{corona}}/kT = f \quad f^2 < N < P^2f^{-2} \quad (12)$$

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

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

The contribution F_{core} accounts for the stretching penalty in the inner, dense region. A crude evaluation of F_{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

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

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

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

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 $P^2f^{-2} < N < P^2f^{1/2}$, 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.

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- [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.