Conformations of star-branched macromolecules

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The dimensions of star-branched macromolecules in dilute solutions were investigated using scaling concepts. The quality of the solvent, the rigidity of star branches, their number and degree of polymerization are taken into account. The relationship between the approaches based on scaling approximations and mean-field approximations is shown. The results obtained are compared to the data of Monte-Carlo simulations and other theoretical results.

(Keywords: polymer solutions; star-branched macromolecules; scaling; grafted chains; expansion coefficient; intramolecular interactions)

INTRODUCTION

The aim of the paper

The size of macromolecular stars in dilute solutions has been investigated in a number of theoretical papers[1-3] but their quantitative results are very contradictory. The present approach to polymer systems based on scaling concepts makes it possible to consider this problem from a new angle[23,24].

In the paper presented here the asymptotic behaviour of the size of long star-branched chains with a large number of branches is investigated. The relationship between the approaches based on scaling approximations and mean-field approximations is shown and the reasons for discrepancies between the results in previously published papers[1-3] are elucidated. The theoretical results are compared to the results of Monte-Carlo calculations[4] and to the experimental data[5,6].

Chain parameters and characteristics

A star consisting of f branches containing n units each will be considered (*Figure 1*). In this case a unit is a part of the chain in the longitudinal dimension, so that l is equal to the chain thickness. In further discussion $l=1$ is taken to be the unit length. The overall degree of polymerization of the star $N=f.n$. Let $p \geqslant 1$ be the parameter of chain rigidity equal to the average number of units in a persistent length (or in a Kuhn segment). The chains with $p \simeq 1$ will be called flexible and those with $p > 1$ will be called stiff.

We will assume that N, f, n and $n/p \gg 1$ restricting ourselves to the asymptotic case, omitting all the numerical coefficients.

In the accepted approximation the mean-square radius of gyration of a star is equal to the mean-square end to end length of each branch. In the simplest case of the Gaussian branches without volume interactions we have

$$R_G^2(\text{star}) \simeq np \approx Npf^{-1} \qquad (1)$$

According to Stockmayer and Zimm[7] the effect of the starlike structure on macromolecular dimensions will be characterized by the ratio (the coefficient of star contraction)

$$g_x = \frac{R_x^2(\text{star})}{R_x^2(\text{linear})} \qquad (2)$$

where R_x^2(linear) is the size of a linear chain of the same p and N, and the subscript x denotes external conditions. For a Gaussian chain we have

$$R_G^2(\text{linear}) \simeq Np \qquad (3)$$

and

$$g_G \simeq f^{-1} \qquad (4)$$

(The coefficient g_G has been calculated over the entire

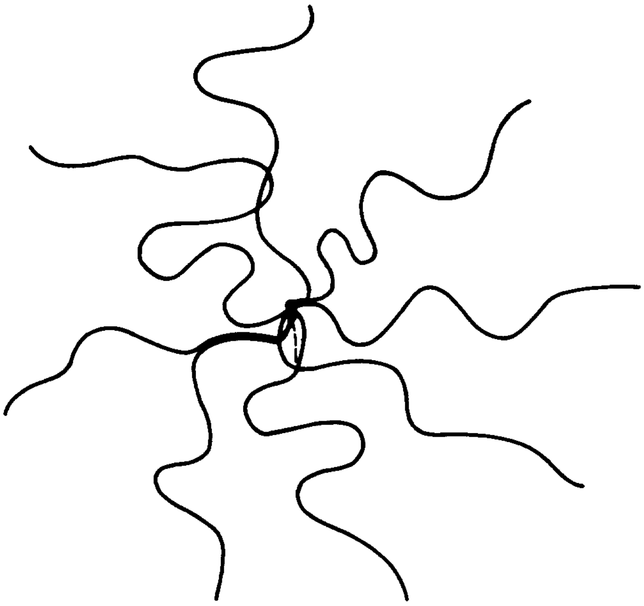

Figure 1 Star-branched macromolecule. The number of branches $f \gg 1$, the length of each branch $n \gg 1$, the overall degree of polymerization $N=f \cdot n$

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range of f in ref. 7, and equation (4) is the limiting value of g_G at $f \gg 1$.)

The coefficient g_x determines the ratio of mean concentrations c of units in the volumes of star-branched and linear chains

$$\frac{c_x(\text{star})}{c_x(\text{linear})} \simeq g_x^{-3/2} \tag{5}$$

For Gaussian chains we have

$$\frac{c_G(\text{star})}{c_G(\text{linear})} \simeq f^{3/2} \tag{6}$$

Volume interactions in chains lead to their expansion compared to the Gaussian size characterized by the expansion coefficient

$$\alpha_x^2(\text{linear}) = \frac{R_x^2(\text{linear})}{R_G^2(\text{linear})} \tag{7}$$

$$\alpha_x^2(\text{star}) = \frac{R_x^2(\text{star})}{R_G^2(\text{star})} \tag{8}$$

to give

$$g_x = g_G \frac{\alpha_x^2(\text{star})}{\alpha_x^2(\text{linear})} \tag{9}$$

Since the unit concentration is higher in star-branched than linear chains, volume interactions have a greater influence on their size and, hence, it might be expected that $\alpha_x^2(\text{star}) \geqslant \alpha_x^2(\text{linear})$ and, correspondingly, $g_x \geqslant g_G$, i.e. the Gaussian limit, equations (4)–(6), overestimate the degree of compression and density of stars.

The principal information required for evaluating the effect of volume interactions on the properties of polymer systems and, in particular, for calculating $\alpha^2(\text{star})$ and g_x is contained in the temperature–concentration diagram of a solution of linear polymers.

Temperature-concentration diagram of a solution of linear polymers

Figure 2a shows the well-known 4–region diagram of a solution of flexible ($p = 1$) linear polymers[8,9] and *Figure 2b* shows its generalization for stiff chains with $p > 1$, i.e. a 6–region diagram recently obtained by one of the present authors[10] (see also ref. 11). Here c is the volume concentration of units in solution, N is the number of units in the chain and $\tau = (T - \theta)/T$ is the relative temperature (we restrict ourselves to the condition $\tau \geqslant 0$). The locations of boundaries of regions and the power dependences of the characteristics of the system are given in *Tables 1* and *2*[8-10]. For the case shown in *Figure 2a* the value of p should be assumed equal to unity. (Since all the power dependences for the regions I_θ and G coincide, the region G has not been considered separately in ref. 10, so that the diagram for stiff chains (*Figure 2b*) was considered to have 5 regions.)

For further discussion it is useful to recollect that the diagrams plotted on the basis of general scaling ideas[13] (introduction of power dependences of the characteristics of the system on its parameters, linked up at the boundaries of different regions) are based on the following assumptions.

(1) The second virial coefficient of interaction between units is proportional to the relative temperature τ[14]; the third virial coefficient is independent of τ; the interactions of higher orders in the concentration range considered are negligible.

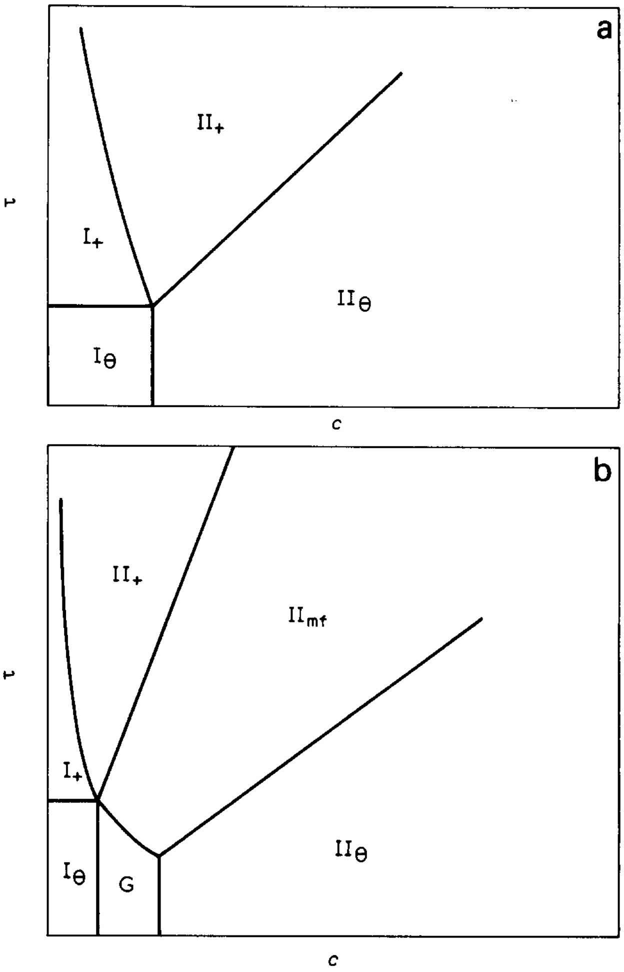

Figure 2 The diagram of state of solution (a) of linear flexible ($p \simeq 1$) polymers and (b) stiff ($p > 1$) polymers. The equations for the boundaries are given in *Table 1*

(2) The size of a linear chain in a dilute solution (regions I in the diagrams) is Gaussian in the tri-critical region I_θ (because both binary and ternary unit interactions are weak). In the region of a good solvent, I_+, the size of the expanded chain is determined by Flory's equation[14]

$$R_+^2 \simeq N^{6/5}\tau^{2/5}p^{2/5} = N^{2\nu_F}(\tau p)^{2\nu_F/3} \tag{10}$$

where $\nu_F = 3/5$.

(3) In region II ($+$, mf, θ) where the chains overlap and the solution is semidilute, the thermodynamic properties of solution are independent of the molecular weight of polymer chains. The thermodynamic unit of solution is a blob, i.e. a chain part in the volume ξ^3 where ξ is the correlation radius of unit density in solution decreasing with solution concentration.

The following conclusions may be drawn from *Figure 2* and *Tables 1* and *2*[8-12]:

(a) For flexible chains ($p = 1$) the mean-field approximation[14] is valid only in θ-regions I_θ and II_θ, in which the binary interactions of units are not important. When binary interactions prevail (regions I_+ and II_+), the mean-field approximation is not valid and leads to the overestimation of the probability of interunit contacts (*Table 2*). For stiff chains ($p > 1$) an additional region II_{mf} exists in which the predominance of binary interactions is combined with the meanfield picture of solution.

Table 1 The equations of the boundaries in the diagrams of state: $x = F(N, p, \tau)$ or $x = F(n, p, \tau)$

Diagram	*Figure 2* $x = c$	*Figure 3* $x = \sigma^{-1}$	*Figure 5* $x = f$	*Figure 7* $x = f$
Regions	Functions $F(N, p, \tau)$ or $F(n, p, \tau)$			
$I_\theta - G$	$N^{-1/2}p^{-3/2}$	$n^{-1}p^{-1}$		
$I_+ - II_+$	$N^{-4/5}p^{-3/5}\tau^{-3/5}$	$n^{-6/5}p^{-2/5}\tau^{-2/5}$		
$G - II_{mf}$	$N^{-1}\tau^{-1}$	$n^{-3/2}p^{1/2}\tau^{-1}$	$n^{-1/2}p^{3/2}\tau^{-1}$	$N^{-1}p^{3}\tau^{-2}$
$G - II_\theta$	$N^{-1/2}$	$n^{-1}p^{1/2}$	$p^{3/2}$	$p^{3/2}$
$II_{mf} - II_+$	$p^{-3}\tau$	$p^{-4}\tau^{2}$	$n^{2}p^{-6}\tau^{4}$	$N^{2/3}p^{-2}\tau^{4/3}$
$II_{mf} - II_\theta$	τ	$p^{1/2}\tau^{2}$	$n^{2}p^{3/2}\tau^{4}$	$N^{2/3}p^{1/2}\tau^{4/3}$
$I_\theta - I_+$	$\tau = N^{-1/2}p^{3/2}$	$\tau = n^{-1/2}p^{3/2}$		

Table 2 The characteristics of the system in different regions of the diagram in *Figure 2*

Characteristic / Region	π/kT	R^2	ξ^2	n_B	$\Delta F_{conc}/kT$	n_B/ξ^3
I_θ	cN^{-1}	Np		N		$N^{-1/2}p^{-3/2}$
G						$N^{-4/5}\tau^{-3/5}p^{-3/5}$
I_+		$N^{6/5}\tau^{2/5}p^{2/5}$				
II_+	$c^{9/4}p^{3/4}\tau^{3/4}$	$N(\tau pc^{-1})^{1/4}$	$(\tau pc^{3})^{-1/2}$	$(\tau^{3}p^{3}c^{5})^{-1/4}$	$N(\tau p)^{3/4}c^{5/4}$	c
II_{mf}	τc^{2}	Np	$\tau^{-1}pc^{-1}$	$\tau^{-1}c^{-1}$	$N\tau c$	$\tau^{1/2}p^{-3/2}c^{1/2}$
II_θ	c^{3}		pc^{-2}	c^{-2}	Nc^{2}	$p^{-3/2}c$

(b) A semidilute solution in region II_+ gives a system of densely packed non-overlapping expanded blobs. For flexible chains this situation is also retained in region II_θ where the blobs are Gaussian. For stiff chains in regions II_{mf} and II_θ the solution is a system of overlapping Gaussian blobs; the degree of overlapping increases with chain stiffness (*Table 2*).

(c) Boundaries of region II_θ are independent of the chain stiffness. For stiff chains a 'Gaussian' region G exists between regions I_θ and II_θ. In this region the thermodynamic properties of solution are determined by the characteristics of chains as a whole (as in region I_θ) in spite of extensive chain overlapping. It should also be noted that the effect of broadening of region II_θ with increasing concentration (boundary equation $\tau \sim c$) is due to the difference between the concentration dependence of probabilities of binary and ternary contacts and is equivalent to the effect discussed by Orofino and Flory[15] in terms of the concentration dependence of the parameter χ.

(d) In all the regions of a semidilute solution II polymer chains may be represented by Gaussian chains of blobs. The number of units in a blob, n_B, is related to its radius ξ according to equation (3) in regions II_θ and II_{mf} and to equation (10) in region II_+, when R^2 is replaced by ξ^2 and N is replaced by n_B.

RESULTS

Layer of grafted chains

Planar matrix. The problem of the size of a star-branched molecule may be formulated as a system of chains (star branches) grafted to a spherical surface of a minimum radius. For clarity it is useful, however, to start from the other limiting case when the matrix is a surface with large radius, i.e. a plane.

Let us consider (according to refs. 16–18 and 23) a system of chains with the degrees of polymerization n grafted to a planar surface with a mean grafting density of $1/\sigma$ where σ is the mean surface area per chain (measured in units $l^2 = 1$). At $\sigma > R^2$ (R^2 is the size of the free chain, from equations (3) and (10)), the polymer layer consists of single coils (within the numerical coefficient) with size R^2 in all directions. At $\sigma < R^2$ the coils overlap and the polymer layer is a semidilute polymer solution in which the polymer concentration c is determined by the layer height H

$$c = \frac{n}{\sigma H} \tag{11}$$

Equation (11) shows directly that polymer chains should stretch to decrease the polymer concentration in the layer. The degree of this stretching and the corresponding concentration in the layer may be determined from the condition of the minimum of free energy of the chain in the layer

$$\frac{\Delta F}{kT} = \frac{\Delta F_{conc}}{kT} + \frac{\Delta F_{el}}{kT} \tag{12}$$

where ΔF_{conc} is the free energy of the chain in a semidilute solution at the concentration c due to binary or ternary interactions of units and ΔF_{el} takes into account chain stretching from the size $R^2(c)$ of a free chain in a semidilute solution to the size H of the chain in the layer

$$\frac{\Delta F_{el}}{kT} \simeq \frac{H^2}{R^2(c)} \tag{13}$$

The power dependences ΔF_{conc} and $R^2(c)$ in all regions of the diagram of the semidilute solution are given in *Table 2*. Using these values and the relationship between H and c according to equation (11), equation (12) is minimized. The result is the diagram of the state of the layer of chains grafted to a plane (*Figure 3*) with the equations for the boundaries (*Table 1*) and power dependences of H and c in regions II of the diagram[16–18,23]

$$\begin{cases} H_+ \simeq H_{mf} \simeq n\left(\dfrac{\tau p}{\sigma}\right)^{1/3} \\ H_\theta \simeq n\sigma^{-1/2}p^{1/4} \end{cases} \tag{14}$$

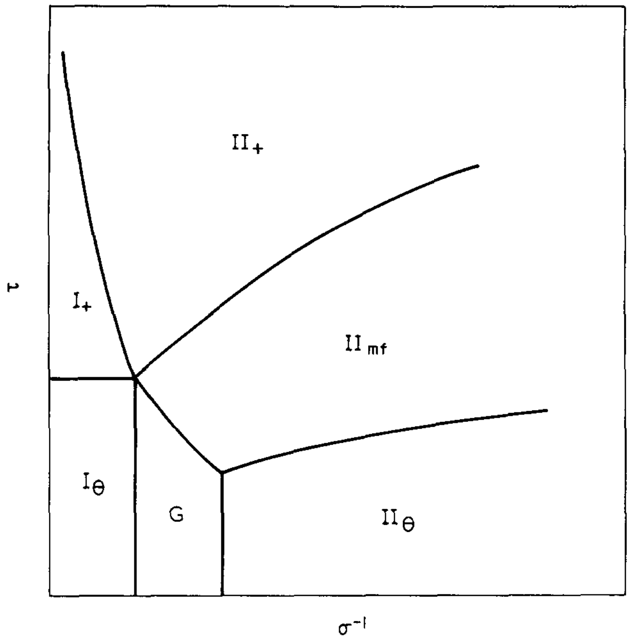

Figure 3 The diagram of state of the planar layer of stiff ($p>1$) polymer chains grafted to the surface, σ^{-1} is the grafting density. The equations for the boundaries are given in *Table 1*. For flexible chains with $p=1$ the regions G and $\mathrm{II}_{\mathrm{mf}}$ disappear and boundaries $\mathrm{I}_\theta-\mathrm{II}_\theta$ and $\mathrm{II}_\theta-\mathrm{II}_+$ appear

$$\begin{cases} c_+ \simeq c_{\mathrm{mf}} \simeq \sigma^{-2/3}(\tau p)^{-1/3} \\ c_\theta \simeq \sigma^{-1/2} p^{-1/4} \end{cases} \tag{15}$$

It is clear from equation (14) that the common structural feature of the layer of chains grafted to a planar surface is their stretching: in region II the height of chains above the surface is proportional to the degree of polymerization n (and increases with the grafting density $1/\sigma$, chain rigidity p and solvent strength τ). The unit concentration in the layer is also an increasing function of the grafting density and is independent of n.

The only exception is the region G for stiff chains under which the chains retain the initial Gaussian size, (equation (3)), in spite of considerable overlapping. This is due to low unit density in stiff Gaussian coils leading to a low value of ΔF_{conc} in the G-region even with chain overlapping.

The structural pattern of the layer of grafted chains in regions II becomes particularly clear if the size of blobs is included in this consideration. By using the data in *Table 2* for $\xi(c)$ and equation (15) for $c(\sigma)$ we find

$$\xi_+ \simeq \sigma^{1/2} \tag{16a}$$

$$\xi_{\mathrm{mf}} \simeq (\sigma \tau^{-1} p^2)^{1/3} \tag{16b}$$

$$\xi_\theta \simeq \sigma^{1/2} p^{3/4} \tag{16c}$$

It can be seen that each chain is a completely extended sequence of blobs

$$H \simeq \frac{n}{n_{\mathrm{B}}} \cdot \xi \tag{17}$$

(where n/n_{B} is the number of blobs in the chain). The situation in the layer of grafted chains for the simplest case when $\xi^2=\sigma$, close-packed lattice of blobs (flexible chains: regions II_+ and II_θ; stiff chains: region II_+) is shown in *Figure 4*. (For stiff chains under conditions II_{mf} and II_θ we have $\xi^2>\sigma$. The overall arrangement of blobs corresponds to the interpenetrating lattices, with the lattice constant ξ, mutually displaced in the direction parallel to the surface of the matrix). At each step a chain of blobs is removed from the matrix. However, the chain is not located in a straight 'tube' with the section σ but, rather in a 'tube' randomly bent in the directions parallel to the surface of the matrix. The chain size in these directions corresponds to that of a Gaussian chain of blobs

$$D \simeq \left(\frac{n}{n_{\mathrm{B}}}\right)^{1/2} \xi \tag{18}$$

to give

$$D_+^2 \simeq n(\tau p)^{1/3} \sigma^{1/6} \tag{19a}$$

$$D^2{}_{\mathrm{mf}} \simeq D_\theta^2 \simeq np \tag{19b}$$

Equations (19a) and (19b) are valid at low degrees of extension $\alpha = H/n \ll 1$; in the general case they contain additional factor κ; at $\alpha^2 \ll 1$ we have $\kappa \simeq C_1 - \alpha^2$ and at high extension, when $(1-\alpha) \ll 1$ we have $\kappa \simeq 1-\alpha$.

On the whole the properties of a layer of grafted chains important to further discussion may be formulated as follows:

(1) For a layer of chains grafted under condition II the direction orthogonal to the matrix surface remains the direction singled out at any large distance from the matrix. Along this direction a chain of blobs is completely extended.

(2) The concentration of units in the layer is determined by the grafting density of chains and is independent of their degree of polymerization.

Spherical matrix. A system of f chains grafted to the outer surface of the spherical matrix of the radius R_{M}[19,23] will now be considered. Let the surface area of grafting per chain be smaller than the size of the free chain, $\sigma_0 \simeq R^2{}_{\mathrm{M}}/f < R^2$, so that the chains overlap forming a common layer (condition II).

According to the results reported in the previous section the existence of the matrix ensures chain stretching normal to it. This makes it possible to separate the total spherical layer into thin quasiplanar layers with variable density of grafting $1/\sigma(r)$ where

$$\sigma(r) \simeq \frac{(R_{\mathrm{M}}+r)^2}{f} \tag{20}$$

Figure 4 Blob picture of the planar layer of grafted flexible ($p \simeq 1$) polymer chains

It has been shown above that the concentration of units in a layer is independent of n and hence it is possible to determine $c(r)$ by substituting the values of $\sigma(r)$ into equation (15). The layer height H was found from the evident condition

$$\int_0^H c(r)(R_M+r)^2 \mathrm{d}r \simeq f\cdot n \qquad (21)$$

Equations (15) and (21) give

$$\mathrm{II}_+\mathrm{II}_{\mathrm{mf}}\colon\ f^{2/3}(\tau p)^{-1/3}[(R_M+H)^{5/3}-R_M{}^{5/3}] \simeq f\cdot n \qquad (22a)$$

$$\mathrm{II}_\theta\colon\quad f^{1/2}p^{-1/4}[(R_M+H)^2-R_M{}^2] \simeq f\cdot n \qquad (22b)$$

In the limit $H \ll R_M$ equations (22a and b) transformed into equation (14) — the case of a planar matrix, i.e. for the chains the size of which is much smaller than that of the matrix its curvature is not revealed.

In our case another limit, $H \gg R_M$, is of interest; for this limit we obtain from equations (22a) and (22b)

$$H_+ \simeq H_{\mathrm{mf}} \simeq n^{3/5}(\tau p f)^{1/5} \qquad (23a)$$

$$H_\theta \simeq n^{1/2}f^{1/4}p^{1/8} \qquad (23b)$$

Before discussing these results we will consider the range of their applicability and construct the diagram of state for grafted chains. The derivation of equations (22a), (22b), (23a) and (23b) was based on equation (15) valid for regions II in *Figures 2* and *3*. Let us prove that the conditions for region II are actually fulfilled over the entire layer of chains grafted to the spherical matrix. Since the area of 'grafting', equation (20), increases with the distance r from the matrix surface to the periphery of the layer, the mean layer density decreases with r

$$c_+ \simeq c_{\mathrm{mf}} \simeq f^{2/3}(\tau p)^{-1/3}(R_M+r)^{-4/3} \simeq \left(\frac{f^2}{\tau p}\right)^{1/3} r^{-4/3} \qquad (24a)$$

$$c_\theta \simeq f^{1/2}p^{-1/4}(R_M+r)^{-1} \simeq f^{1/2}p^{-1/4}r^{-1} \qquad (24b)$$

(Right-hand sides of equations (24a) and (24b) are valid at $r \gg R_M$.) The minimum values of density on the periphery of the layer $r \approx H$ are (for $H \gg R_M$)

$$(c)_{\min} \simeq (c_{\mathrm{mf}})_{\min} \simeq n^{-4/5}(\tau p)^{-3/5}f^{2/5} \qquad (25a)$$

$$(c_\theta)_{\min} \approx n^{-1/2}p^{-3/8}f^{1/4} \qquad (25b)$$

From *Table 1* it follows that these densities correspond to regions II in *Figures 2* and *3* when the numbers of grafted chains f are

$$f_+ \geqslant \mathrm{I} \qquad (26a)$$

$$f_{\mathrm{mf}} \geqslant p^{3/2}n^{-1/2}\tau^{-1} \qquad (26b)$$

$$f_0 \geqslant p^{3/2} \qquad (26c)$$

These results together with the data of *Table 1* are sufficient to obtain[19,23] the diagram of state for the layer of chains grafted to a small spherical matrix, *Figure 5*. As the above diagrams (*Figures 2* and *3*) contain the G-region (in which all chains retain the free state characteristics) if the chains rigidity, $p > \mathrm{I}$, is taken into account. The G–II boundaries are given by the equality sign in equations (26a), (26b) and (26c).

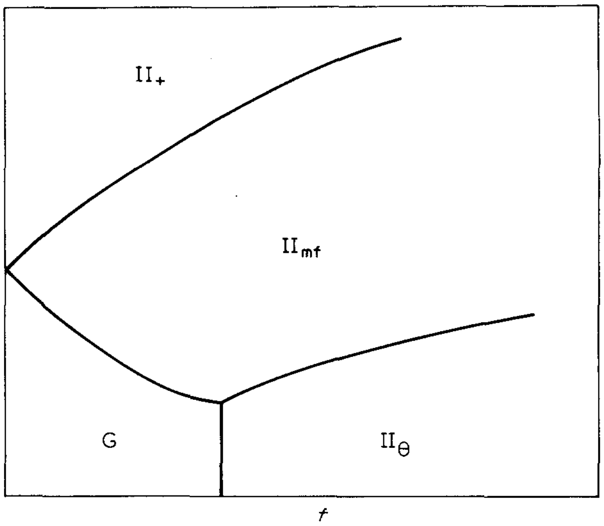

Figure 5 The diagram of state of stiff ($p > 1$) polymer chains grafted to a small spherical matrix, f is the number of the grafted chains. The equations for the boundaries are given in *Table 1*. For flexible chains with $p = 1$ the regions G and $\mathrm{II}_{\mathrm{mf}}$ disappear and the boundary $\mathrm{II}_\theta - \mathrm{II}_+$ appears

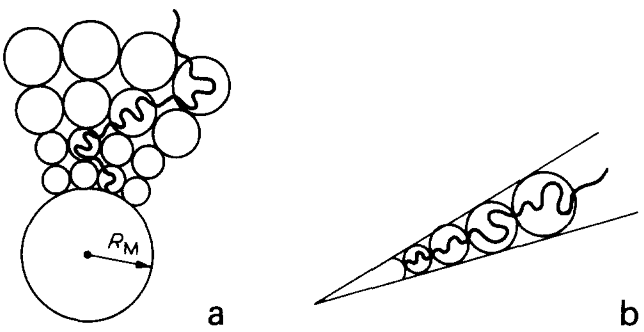

Figure 6 (a) Blob picture of the spherical polymer layer for flexible ($p \simeq 1$) chains and (b) a single chain placed in its cone with the straightened axis and the angle $\sim f^{-1}$

In regions II, i.e. at $f > f_{\min}$, the chains are stretched according to equations (23a) and (23b) from which it follows that this stretching is independent of the size of the matrix (when it is small, $R_M \ll H$). It can be seen from a comparison of equations (14), (23a) and (23b) that the extension of grafted chains is much less pronounced for a spherical than for a planar matrix. Chains grafted onto a small sphere retain the dependence on n the characteristic of free chains: $H \sim n^{1/2}$ or $n^{3/5}$. Similarly, the character of radical decrease in density: $c(r) \sim r^{-1}$ or $r^{-4/3}$ according to equations (24a) and (24c) at $r \gg R_M$ reflects the usual shape of the binary correlation function of the unit density $g(r)$ in a free chain[8,13].

Figure 6a shows the blob picture of the layer of chains grafted onto the spherical matrix under conditions II_+. The concentration of units decreases on passing from the matrix surface to the periphery of the layer (according to equation (24)) and the size of blobs increases (see the relationship between ξ and c in *Table 2*). Each chain is represented by a radially ordered system of growing blobs, i.e. the chain is 'placed' in a cone with the angle $\sim 1/f$. As is the case for grafting onto a plane, the tangential order is absent, i.e. the cone axis is tangentially bent. *Figure 6b* shows one chain in its cone with the straightened axis. The increase in the surface area of the cone section with increasing distance from the matrix surface leads not only to the radical decrease in unit concentration but also to the corresponding decrease in the local degree of chain extension (see previous section).

It should be noted that although the concentration of units decreases with increasing distance from the matrix surface, the main part of units lies in the peripheral part of the sperical layer. Hence, it is easy to determine from equations (24a) and (24b) that in region II half of all the units occupy the outer part of the layer (the thickness of which is not greater than 1/3 of its total height). Consequently, the properties of the layer are determined to a considerable extent by its outer part. It is precisely for this reason that we determined the boundaries of regions in the diagram in *Figure 5* on the basis of characteristics of the periphery of the layer (see ref. 19 for greater detail).

Star size

Coefficients of star contraction. Equations (23a) and (23b) are able to determine the size H_x of chains grafted onto a small matrix and also determines the size $R_{x(\mathrm{star})}$ of the star as a whole (in an asymptotic approximation within the numerical coefficients). Introducing into the equations the degree of polymerization of the star $N = nf$ we have[23]

$$R_+(\mathrm{star}) \simeq R_{\mathrm{mf}}(\mathrm{star}) \simeq N^{3/5}(\tau p)^{1/5} f^{-2/5} \quad (27a)$$

$$R_\theta(\mathrm{star}) \simeq N^{1/2} p^{1/8} f^{-1/4} \quad (27b)$$

$$R_G(\mathrm{star}) \simeq N^{1/2} p^{1/2} f^{-1/2} \quad (27c)$$

The diagram of state of the star obtained from the diagram in *Figure 5* by replacing n with N/f is shown in *Figure 7*. To avoid confusion, it should be emphasized that the diagram in *Figure 7* characterizes a star in a dilute solution and region II takes into account the high intramolecular concentration (but does not take into account the interstar interactions).

If we apply the definition of star contraction coefficient from equation (2), it can be seen in *Figure 7* that generally speaking at a given N, p and τ the thermodynamic state of star consisting of f branches may not coincide with the state of a linear chain ($f = 1$). In principle, for a flexible chain three variants are possible (both chains, a linear chain and a star, are under the θ-conditions, in the region of a good solvent or the mixed case). For a stiff chain the number of variants increases to five (if regions II_+ and $\mathrm{II}_{\mathrm{mf}}$ in which the size of stars coincides are combined). Equations (3), (10) and (27a)–(27c) are used to find all possible values of the contraction coefficient $g_{\mathrm{x/y}}$ where x and y denote the regions of the states of a star and a linear chain, respectively, subscript x replaces x/y and the state II_{mf} is included into II_+

$$g_\theta \simeq p^{-3/4} f^{-1/2} \quad (28a)$$

$$g_+ \simeq f^{-4/5} \quad (28b)$$

$$g_{\theta/+} \simeq N^{-1/5} \tau^{-2/5} p^{-3/20} f^{-1/2} \quad (28c)$$

$$g_G \simeq f^{-1} \quad (28d)$$

$$g_{+/\theta} \simeq N^{1/5} \tau^{2/5} p^{-3/5} f^{-4/5} \quad (28e)$$

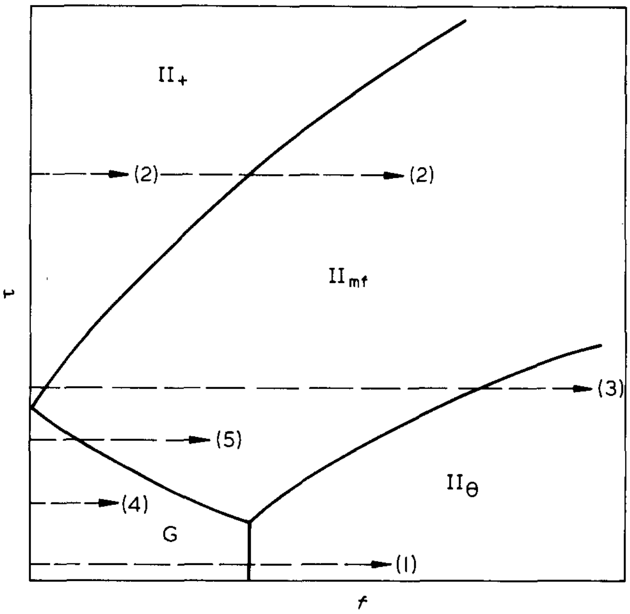

Figure 7 The diagram of state of an isolated star-branched macromolecule, $p > 1$. The equations for the boundaries are given in *Table 1*. Figures in brackets correspond to the letters in equation (28): $a = 1$, $b = 2$, etc. For flexible chains with $p = 1$ the regions G and $\mathrm{II}_{\mathrm{mf}}$ disappear and boundary $\mathrm{II}_\theta - \mathrm{II}_+$ appears

The regions of the validity of each coefficient are shown in *Figure 7* by numbers in brackets corresponding to the letters in equations (28a)–(28e): $a = 1$; $b = 2$, etc.

Figure 8 shows the change in the star contraction coefficient g with increasing number of branches f in a star and with increasing strength of the solvent τ (horizontal and vertical sections of the diagram in *Figure 7*). Equations (28a)–(28e) and *Figure 8* show that stiffness plays an important part in the behaviour of stars. For flexible macromolecules the degree of contraction is always lower than the limiting Gaussian value, g_G, and for stiff macromolecules the region of maximum contraction, g_G, applies. For flexible stars the degree of contraction is always the non-increasing function of solvent strength. For stiff macromolecules this type of dependence is observed only if the number of branches is relatively large ($f > p^{5/2}$) and at a lower f, $g(\tau)$ can increase with τ (of course, at all τ values $g < 1$).

Expansion coefficients of stars

Let us now consider the expansion of stars with respect to their Gaussian size (equation (8)). Equations (3), (8), (10) and (27a)–(27c) yield expansion coefficients in various regions of the state of stars (region II_{mf} in *Figure 7* is combined with II_+)

$$\alpha_+^2 \simeq N^{1/5} \tau^{2/5} p^{-3/5} f^{1/5} \quad (29a)$$

$$\alpha_\theta^2 \simeq p^{-3/4} f^{1/2} \quad (29b)$$

$$\alpha_G^2 \simeq 1 \quad (29c)$$

Equation (29a) represents the expansion of a star in a good solvent. It is clear that the square of the expansion coefficient of a star is higher by a factor of $f^{1/5}$ than for an equivalent linear chain. Equation (29b) shows that a star expands not only in the region of a good solvent but also in the θ-region. In this case, however, the expansion coefficient is independent of N and is determined only by

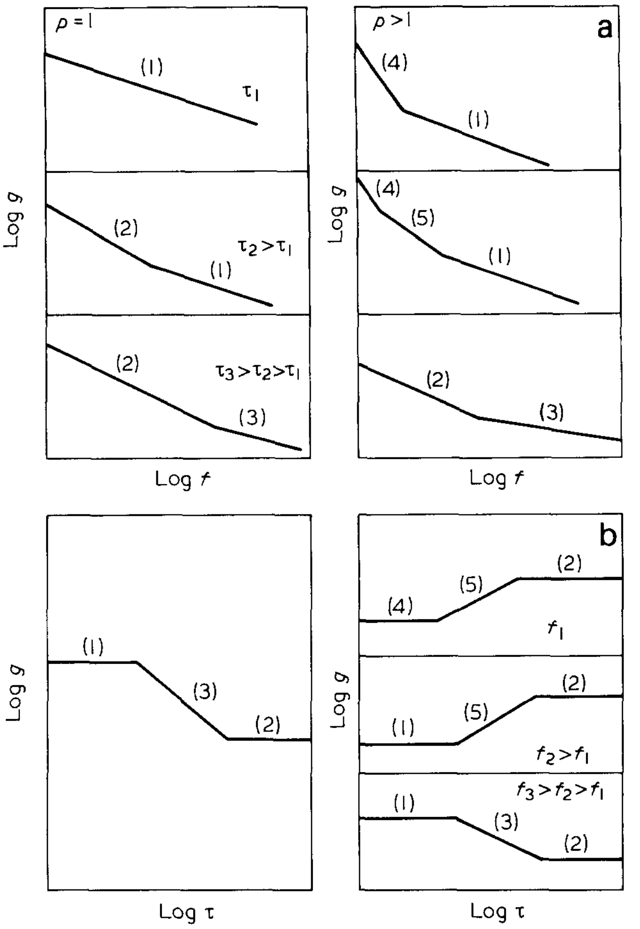

Figure 8 (a) The dependence of the star contraction coefficient on the number of star branches and (b) the solvent strength for flexible and stiff chains. Figures in brackets correspond to the letters in equation (28)

the number of branches $\alpha_\theta^2 \sim f^{1/2}$. For stiff macromolecules with a moderate number of branches, $f < p^{3/2}$, the stars retain the Gaussian size $\alpha_G^2 = 1$.

Note that at any fixed value of τ the following condition is fulfilled: $\alpha^2(\text{star}) \geqslant \alpha^2(\text{linear})$ where the sign of equality can occur only for stiff macromolecules.

In experiments the relative chain expansion when the solvent strength increases is often determined. The relative expansion is characterized by the coefficients

$$\alpha_+^2/\alpha_\theta^2 \simeq N^{1/5}\tau^{2/5}p^{3/20}f^{-3/10} \tag{30a}$$

$$\alpha_+^2/\alpha_G^2 \simeq N^{1/5}\tau^{2/5}p^{-3/5}f^{1/5} \tag{30b}$$

where equations (30a) and (30b) are valid at $f > p^{3/2}$ and $f < p^{3/2}$, respectively. Hence, for flexible macromolecules the relative expansion of a star is always less by a factor of $f^{-3/10}$ than that for a linear chain, whereas for stiff macromolecules the dependence of relative expansion coefficient on the number of branches f passes through a maximum near $f \simeq p^{3/2}$.

DISCUSSION

Star size. Scaling and the mean field approximations

The method for the determination of size of a polymer chain (by minimization of equation (12)) has been proposed by Flory[14] who used the mean-field approximation for the component F_{conc}. Let us apply this approximation to the star-branched molecule as a whole. In this case it is sufficient to consider the mean unit density in a coil

$$\bar{c} \simeq \frac{N}{R^3} \tag{31}$$

without analysing its change inside the coil. For regions of a good and a θ-solvent in which the contributions of binary and ternary interaction, respectively, prevail, the free energy is given by

$$\frac{\Delta F}{kT} \simeq f \cdot \frac{R^2}{Np/f} + \tau \cdot \frac{N^2}{R^3} \quad \min \tag{32a}$$

$$\frac{\Delta F}{kT} \simeq f \cdot \frac{R^2}{Np/f} + \frac{N^3}{R^6} \quad \min \tag{32b}$$

(where $R_G^2 = Np \cdot f^{-1}$, from equation (1)). The factor f in the first term takes into account the necessity for stretching of all f branches when the star expands. It can be easily seen that as a result of minimization equations (27a) and (27b) are obtained as well as equation (27c) at $f < p^{3/2}$ if the condition $R^2 \geqslant R_G^2$ is taken into account. These equations may be written in the form emphasizing the relationship between indices

$$R_+ \simeq N^{\nu_F}(\tau p)^{\nu_F/3} f^{-2\nu_F/3} \tag{33a}$$

$$R_\theta \simeq N^{\nu_\theta} p^{\nu_\theta/4} f^{-\nu_\theta/2} \tag{33b}$$

where $\nu_F = 3/5$ and $\nu_\theta = 1/2$.

Hence, the detailed analysis carried out in the Results section yields the mean-field size of starlike chains. Naturally, this is not surprising if the conditions corresponding to regions II_{mf} and II_θ of the state diagram in which the mean-field approximation is valid, are satisfied. It is important, however, that in the scaling region II_+ the mean-field value of the star size is obtained (according to equations (27a)–(27c) we have $R_+ = R_{\text{mf}}$).

To analyse the reason for this coincidence the free energy of a star in scaling region II_+ will be considered. According to equation (12) and *Table 2*, by using the evaluation of ΔF_{conc} the mean density $\bar{c}$, equation (31), we have:

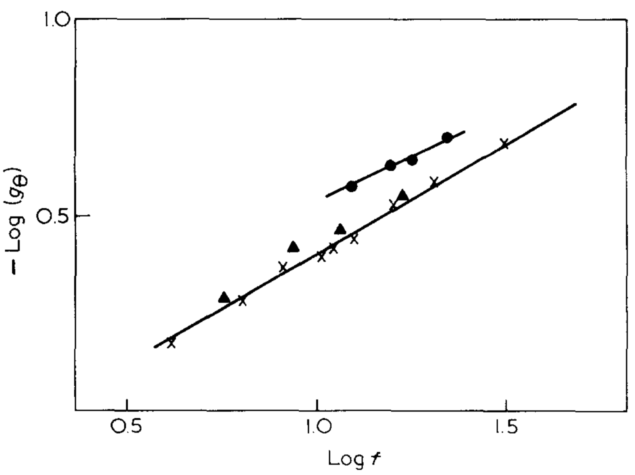

Figure 9 The log–log plot of the star contraction coefficient g *versus* the number of star branches f under θ-conditions: ×, the Monte Carlo simulation[4]; ●[5] and ▲[6], the experimental data. Slopes of straight lines $\gamma_\theta = 0.5$–0.6

$$\frac{\Delta F}{kT} \simeq f \cdot \frac{R^2}{R^2(c)} + \tau N \left(\frac{N}{R^3}\right)^{5/4} \qquad (34a)$$

$$f \frac{R^2}{Np/f} \left(\frac{N}{R^3}\right)^{1/4} + \tau N \left(\frac{N}{R^3}\right)^{5/4} \qquad \text{min} \qquad (34b)$$

(Analysis shows that the use of $\bar{c}$ in equation (34) is permissible for a wide class of intramolecular distributions $c(r)$, in particular for the power law decreasing functions as in equation (24).)

It is clear that equations (34a) and (34b) differs from equation (32a) only in the factor $(N/R^3)^{1/4}$, which does not affect the result of minimization and gives the mean-field value of R_+.

This result is due to the fact that (as has been indicated in the Introduction), the Flory mean-field radius of a linear chain $R^2 \sim N^{6/5}$ (see equation (10)) is used as one of the basic points for the diagram of state (*Figure 2*) and scaling relations (*Table 2*). Equation (10) is manifested in power dependences of all characteristics. In the case of linear chains it requires, in particular, such a form of $R^2(c)$ which ensures the equivalence of equations (32a) and (34). It is easy to see that if this equivalence is predetermined for a linear chain, it is also retained for a star-like macromolecule. Thus the simplest scaling procedure transfers the assumption of the mean-field dimensions from linear to star-like chains.

Moreover it can be shown that this conclusion is of a more general character and refers to the dimension of an isolated chain at any type of perturbations or restrictions introduced (e.g. for a chain in a slit, a branched chain, etc.). In the framework of the scaling scheme based on equation (10) the mean-field values will always be obtained.

Comparison with other results

We will first compare our results with those in theoretical papers[1–3,24], published in the last decade (see the list of earlier papers in ref. 1) and will consider the expansion coefficient of stars determined from equation (8) with respect to Gaussian size.

Three expressions were obtained for α_x^2 (equation (29)) in various regions of the diagram of state for stars (*Figure 7*). The Gaussian region is present only for stiff macromolecules with $p > 1$. The stiffness of star-branched macromolecules has not been taken into account previously and hence the existence of the region G in which expansion is absent, $\alpha_G^2 = 1$, has not been predicted.

As to the expansion coefficient α_+^2 and α_θ^2, since R_+^2 and R_θ^2 have the mean-field values, it could be expected that our data for flexible chains at $p = 1$ would be in complete agreement with the results of theories based on the mean-field approximation. In particular, the work of Candau *et al.*[1] has been carried out within this approximation according to Flory's scheme[14]. In fact, the power dependences of α on N and τ are in complete agreement with those obtained in ref. 1 (as well as in refs. 2, 3 and 24): $\alpha_\theta^2 \sim N^0$, $\alpha_+^2 \sim N^{1/5}\tau^{2/5}$.

However, it was unexpectedly found that we obtained new values of exponents β determining the dependence of α^2 on the number of branches f in a star,

$$\alpha_x^2 \sim f^{\beta_x} \qquad (35)$$

Moreover, as can be seen from *Table 3*, it was found that an entire set of theoretical values of these exponents is reported in the literature[1–3,24]. Evidently, to confirm our results it is advisable to analyse the reason leading to other values of β_x.

We will first consider the results reported in ref. 1 obtained for the mean-field approximation by minimizing the free energy (equation (12)). This free energy takes into account binary or ternary interactions. This is also done in equations (32a) and (32b) in the paper presented here. The discrepancy between the equations in ref. 1 and equations (32a) and (32b) is related to the term $\Delta F_{\text{el}}/kT$. Candau *et al.*[1] assumed that $\Delta F_{\text{el}}/kT = R^2/R_G^2$ (by analogy with a linear chain). In the present work this term is greater by a factor f.

It can easily be seen that in the former case the stretching of only one branch is taken into account, whereas the expansion of a star is related to the stretching of all f branches. We believe that the consideration of a star as a system of grafted chains makes this conclusion particularly clear.

As a result of the underestimation of ΔF_{el} Candau *et al.*[1] have overestimated the dependence of expansion on f, i.e. they have obtained excessively high values of β_+ and β_θ (3/5 and 3/4 instead of 1/5 and 1/2, respectively, see *Table 3*). The values of the exponent $\gamma_x = 1 - \beta_x$ in the coefficient of star contraction

$$g_x \sim f^{-\gamma_x} \qquad (36)$$

became too low, see equations (2) and (28a)–(28e) and *Table 3*.

The same values of β_θ and γ_θ in Khokhlov's paper[2] are due to the repetition of the same error as in ref. 1. Having shown that for a star the corrections due to the replacement of monomers (as interaction units) by quasi-monomers are not important, he reproduced the mean field results of ref. 1 for the θ-region using the same expression for ΔF_{el}.

Table 3 The exponents β_x and γ_x in the dependences $\alpha_x^2 \sim f^{\beta_x}, g_x \sim f^{-\gamma_x}$, eqs. (35), (36). Index x indicates the region on the diagram of state of star-like macromolecules, *Figure 7*

	Theoretical values					
		Candau, Rempp,	Khokhlov		Daoud, Cotton	Experimental data and simulations,
Exponent	Present work	Benoit, 1	2	3	24	4–6
β_θ	1/2	3/4	3/4	1	1/2	–
β_+	1/5	3/5	–3/5	–	1/5	–
β_G	0	–	–	–	–	–
γ_θ	1/2	1/4	1/4	0	1/2	0.5–0.6
γ_+	4/5	2/5	8/5	–	4/5	–
γ_G	1	–	–	–	–	–

Even higher θ-expansion ($\beta_\theta = 1$) is obtained in ref. 3. This was due to the complete neglection of the term ΔF_{el}. In ref. 3 the θ-size of the macromolecule was determined with the aid of globules. In the scheme proposed in ref. 3 the continuity of changes in macromolecular dimensions in the second-order phase transition coil–globule[20] is used and the power asymptotics of the size of the globule R_- and the transition point τ_c should be known. By analogy with a linear chain[20] the author completely neglects the term ΔF_{el} in the free energy of the globule and as a result the values $R_- = (N/|\tau|)^{1/3}$ and $\tau_c = N^{-1/2}$ as well as the θ-size of the star $R_\theta = N^{1/2}$ become the same as for a linear chain and are independent of f (the number of branches).

Correspondingly, the coefficient of star contraction appears equal to unity ($\gamma_\theta = 0$, *Table 3*), i.e. the transition from a linear to a star-like chain does not change its θ-dimensions.

A similar and just as paradoxical result has been obtained[3] for another system: a two dimensional θ-coil the volume of which was found to be equal to the θ-volume of a three dimensional coil. We suppose that the estimations of τ_c for these systems should be revised taking into account the value of ΔF_{el} (see also ref. 21).

In contrast, for α_+^2 Khokhlov[2] has obtained a decrease in expansion with f, which leads to an increase in star contraction as compared to the Gaussian chain (compare $\gamma_+ = 8/5^2$ and $\gamma_G = 1$, equation (4) and *Table 3*), although, as has been indicated in the Introduction, the degree of star contraction should be maximum for a Gaussian chain. According to our data, the increase in f leads to a decrease in the relative rather than absolute expansion coefficient (equations (30a) and (30b)).

After the present paper had been prepared for publication (some of its results have been briefly stated in ref. 23) a paper by Daoud and Cotton[24] dealing with the conformations of flexible star-like macromolecules and based on the scaling concept was published. As can be seen from *Table 3*, the values of β_+ and β_θ obtained in ref. 24 are in complete agreement with the results of the present work at $p = 1$. This agreement seems important because the specific applications of scaling formalism in this work and in ref. 24 were different. We proceeded from the analysis of a system of grafted chains passing from a planar to a spherical matrix and using the blob picture of the system only as an illustration. The authors of ref. 24 have based their concept on the blob picture of a semi-dilute solution restricting themselves to the case of flexible ($p = 1$) chains. On the other hand, the structure of the compact nucleus of star-like macromolecules has been studied in greater detail in ref. 24. If the analysis carried out in this reference is extended to the case $p > 1$, it follows that the diagram in *Figure 7* should be supplemented with the boundary $f = N^{2/3}p^{1/2}$. To the right of this boundary is located the region of densely packed stars for which $R = N^{1/3}$.

Now we will compare these results with both the real experimental results[5,6] and those of a computer simulation[4]. *Figure 9* shows the dependences on f of the coefficient of star contraction under the θ-conditions (θ-conditions for linear chains) observed in refs. 4–6. Although the experimental values of $f = 4$–20 are not very high, the slopes of straight lines $\gamma_\theta = 0.5$–0.6 are in good agreement with the value obtained in the present work, $\gamma_\theta = 0.5$. We could not find similar experimental dependences for the case of good solvent. The comparison with unpublished data carried out in ref. 24 confirms the values of β_+ and γ_+ obtained in ref. 24 and in the present work (*Table 3*).

Two-dimensional stars

The conclusion drawn earlier, that the mean-field approximation is applicable (in the framework of primitive scaling) to the estimation of the size of macromolecules determining the intramolecular concentration of units; also makes it possible to find the star size in the two-dimensional case (adsorbed chains and chains in a slit). For this purpose it is sufficient to replace in the second term on the right-hand side of equations (32a) and (32b) the tri-dimensional volume R^3 by a two-dimensional volume R^2.

For the region of a good solvent and the θ-region the results, as previously, are described by equations (33a) and (33b) in which the values of the index correspond to another space dimensionality $d = 2$, i.e. $\nu_F = 3/4$ and $\nu_\theta = 2/3$[21,22].

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