Temperature–concentration diagram for a solution of star-branched macromolecules

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The temperature–concentration diagram of a star-branched macromolecule solution was constructed using scaling concepts. The quality of the solvent, solution concentration, the rigidity of star branches, their number and degree of polymerization were taken into account. The diagram obtained contains three regime types: I_x—isolated stars in a dilute solution; II_x—a semidilute solution of star branches (subscript characterizes the volume interactions); and III—the close packed system of impermeable (or almost impermeable) stars. Quasiglobular regime III is characterized by the universal dependence of star size on the concentration of the solution c and degree of polymerization N: $R \sim (N/c)^{1/3}$ independently of the quality of the solvent.

(Keywords: polymer solution; star-branched macromolecules; scaling; temperature-concentration diagram; segregated structure)

INTRODUCTION

In our preceding paper[1] and in a paper by Daoud and Cotton[2] the scaling theory of conformations of star-branched macromolecules in a dilute solution has been developed. The purpose of the present paper is to generalize the results for the case of semidilute solution and to construct the temperature–concentration (τ–c) diagram of state for a solution of star-branched macromolecules.

Analysis of the behaviour of stars in a semidilute solution will proceed from the results obtained for isolated stars. A brief survey of these results is now given. The new theoretical papers on star conformations that have appeared since our earlier publication[1] will also be considered.

Star parameters and characteristics

Star-branched macromolecules consisting of f branches with n units in each branch and overall degree of polymerization $N = nf$ (*Figure 1*) will be considered. A chain sequence of length a_0 equal to the chain thickness d subsequently taken as unit length is chosen as the monomer unit. Let the asymmetry parameter of a chain segment be $p = a/d \geqslant 1$ (a is the length of the Kuhn segment) and let us call chains with $p = 1$ 'flexible' and those with $p > 1$ 'stiff'. We will assume that f, n and $n/p \gg 1$ and restrict ourselves to the consideration of asymptotic dependences omitting all the numerical coefficients. The mean-square radius of gyration R_x is taken as the characteristic of the star size. In the approximation used R_x is equal to the mean-square end-to-end distance of each branch. Subscript x determined the external conditions (see next section on 'Diagram of state and conformations of isolated stars').

For isolated stars, two relative size characteristics are also considered: the coefficient of star contraction (with respect to a linear chain with the same N)

$$g_x = \frac{R_x^2(\text{star})}{R_x^2(\text{linear})} \sim f^{-\gamma_x} \tag{1}$$

and the coefficient of swelling with respect to the Gaussian ($x = \mathrm{G}$) size

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

On the right-hand side of equations (1) and (2) these coefficients are shown as power dependences (which corresponds to the asymptotic limit) on the number of branches only because it is the dependences on f that are the subject of discussion (for further details see ref. 1).

It follows from (1) and (2) that exponents β and γ are related to each other by a linear equation

$$\beta_x + \gamma_x = \gamma_G = 1 \tag{3}$$

where it is taken into account that in the approximation used $g_G \sim f^{-1}$ (refs. 1 and 3). Further, since volume concentration of units in stars is higher than in linear chains, volume interactions (repulsion) should always affect the size of stars more markedly than those of linear chains. Hence, the Gaussian value $\gamma_G = 1$ is the limiting value, and if volume interactions exist, it might be expected that

$$0 < \gamma_x < 1 \tag{4}$$

where the left-hand inequality is evident.

Diagram of state and conformations of isolated stars

As already mentioned, the theory of conformations of isolated stars has been developed elsewhere[1,2]. Although

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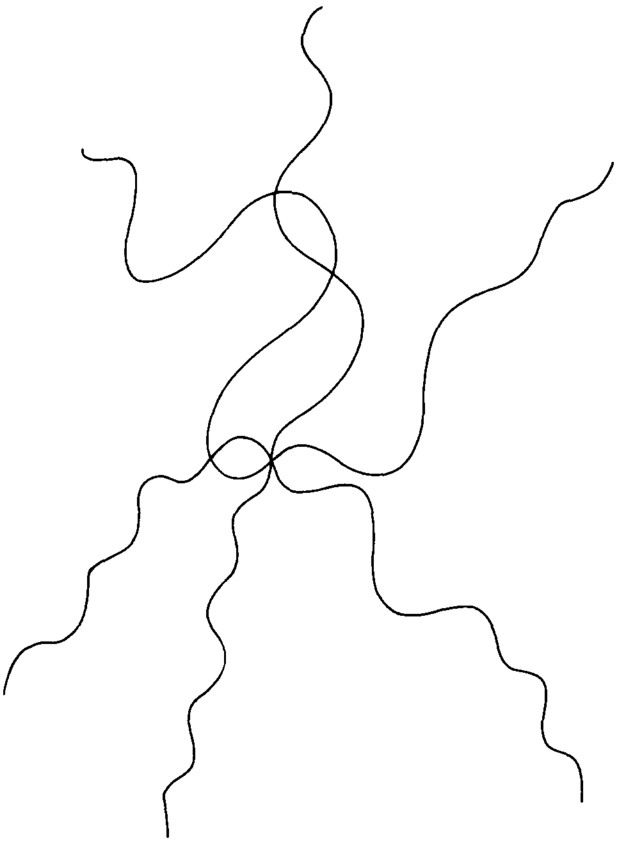

Figure 1 Star-branched macromolecule. Branch number $f>1$, length of each branch $n \gg 1$, overall degree of polymerization $N = fn$

the specific application of scaling formalism in these papers differ slightly, the results coincide completely. Moreover, they are complementary to each other because ref. 2, in contrast to ref. 1, considers only the case $p=1$, but on the other hand, more attention has been devoted to the structure of the dense nucleus of the star.

Figure 2 shows a diagram of state for isolated stars reproducing that in ref. 1 (with additions according to ref. 2). The diagram is based on a model for a layer of semi-stiff chains grafted with one end onto an impermeable spherical surface (star nucleus)[4,5] and on the well known relationships in the theory of semidilute solutions of macromolecules[6-9]. The consequence of the model is the conclusion about the power increase in the correlation radius of density (blob size) with increasing distance from the nucleus.

The diagram of isolated stars in *Figure 2* in the case of a flexible chain $p=1$ contains three regions of state I_x with $x = \Theta, +, d$. In the region I_Θ the star conformation is determined by ternary interactions of units; I_+ is the scaling region of pair interactions (a good solvent); I_d corresponds to a star consisting only of a dense nucleus. For semi-stiff chains, $p>1$, a Gaussian region I_G and the mean field region of pair interactions I_{mf} appear (for further details see ref. 9).

To avoid confusion it should be noted that in this paper we denote the regions of state in diagrams of *Figure 2* by I_x in order to emphasize the fact that they refer to isolated stars (symbols II_x in ref. 1 emphasized the relationship of the states of a star to those of a semidilute solution of linear chains; for further details see ref. 1).

Table 1 summarizes data on the size R_{x0} of isolated stars (subscript 0), the coefficients of star contraction g_{x0} and swelling α_{x0}^2 as well as intramolecular characteristics: the average concentration of units $\bar{c}_{x0}$ in a star and the law of radial decrease in concentration $c_{x0}(r)$. These results are considered in detail in ref. 1 and here only the following four points will be noted.

(1) The stars are virtually always (at $\tau \geqslant 0$) in the swollen state, $\alpha_{x0}^2 > 1$. The only exception is the Gaussian region of states I_G. However, this region exists only for stars with a small number of semi-rigid branches $f < p^{3/2}$ near the Θ-point.

(2) The data in *Table 1* yield the values of the exponent γ in equation (1)

$$\gamma_x = \begin{cases} \frac{4}{5} & x = +, \mathrm{mf} \\ \frac{1}{2} & x = \Theta \end{cases} \tag{5}$$

in complete agreement with the estimations in inequality (4). It has been shown[1,2] that these values are in good agreement with both the experimental data and the Monte Carlo results. The results have been compared in detail with those of other theories in ref. 1. and the reasons for the discrepancies have also been analysed. It has been shown that the values of exponents γ_x in equation (5) may be directly obtained according to Flory's scheme in the mean-field approximation.

Some papers have recently appeared[10,11] in which the size of star-branched macromolecules and, correspondingly, exponents γ_x have been calculated on the basis of the renormalization-group approach. In ref. 10 the use of the RG method to within the second order in the ε expansion has yielded $\gamma_\Theta = 1$ and $\gamma_+ = 2\nu \simeq \frac{6}{5}$. These results

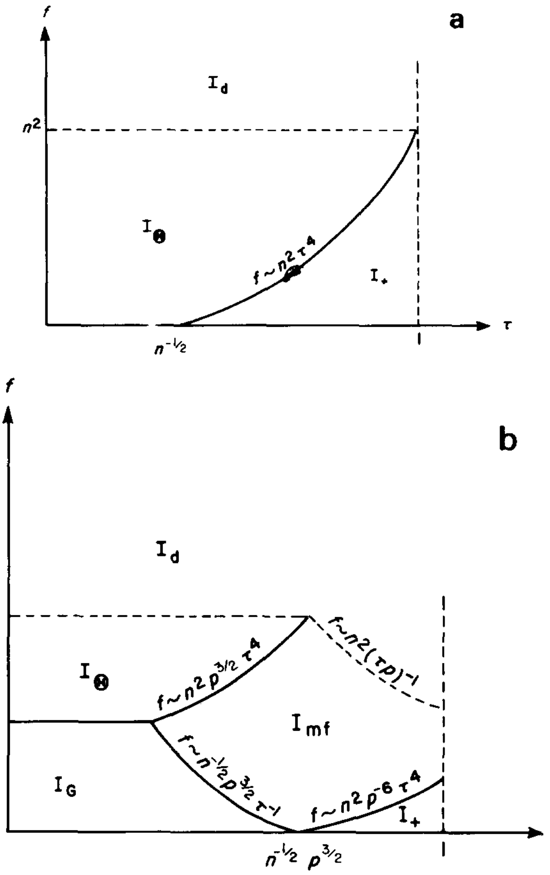

Figure 2 Diagram of state of an isolated star-branched macromolecule: (a) flexible chains, $p=1$; (b) semi-stiff chains, $p>1$. Equations of region boundaries are given in the figures

Table 1 The parameters of isolated stars

x	R_{x0}	g_{x0}	α^2_{x0}	$\bar{c}_{x0}$	$c_{x0}(r)$
+, mf	$N^{3/5}(\tau p)^{1/5}f^{-2/5}$	$f^{-4/5}$	$N^{1/5}\tau^{2/5}p^{-3/5}f^{1/5}$	$N^{-4/5}(\tau p)^{-3/5}f^{6/5}$	$f^{2/3}(\tau p)^{-1/3}r^{-4/3}$
Θ	$N^{1/2}p^{1/8}f^{-1/4}$	$p^{-3/4}f^{-1/2}$	$p^{-3/4}f^{1/2}$	$N^{-1/2}p^{-3/8}f^{3/4}$	$f^{1/2}p^{-1/4}r^{-1}$
G	$N^{1/2}p^{1/2}f^{-1/2}$	f^{-1}	1	$N^{-1/2}p^{-3/2}f^{3/2}$	$fp^{-1}r^{-1}$

are inconsistent with estimations in inequality (4) and seem to be erroneous. Since in ref. 11 a scheme of the RG method is used in which only the first order in the ε expansion is taken into account and which is inferior to that in ref. 10 with regard to the certainty of evaluation of the exponents, we suppose that at present the results in *Table 1* and equation (5) are the most reliable of all.

(3) Let us consider the radial dependence of density in a star. In the centre of the star a region with a constant high density exists: the nucleus in which the chains are extended according to the law $r_d \sim n_d$, where the nucleus size is $r_d \sim f^{1/2}$ and n_d is the number of units in a branch in the nucleus. Further, the structure may be represented by a system of spherical layers consisting of blobs growing in the radial direction (see *Figure 6* below and for further details see refs. 1 and 2). Near the nucleus the concentration is high and the blobs are Gaussian. The radial decrease in concentration in this region is described by the relationship $c(r) \sim r^{-1}$ (*Table 1*). As the concentration decreases further, the significance of pair interactions between units increases, the blobs become swollen and the decrease in concentration is described by the relationship $c(r) \sim r^{-4/3}$ (*Table 1*). At given $f > p^{3/2}$, τ and p values this concentration profile is universal and the boundaries of spherical regions do not depend on n. However, at low n values the star does not grow up further than the size of the nucleus and the occurrence of all three internal regimes requires relatively high n values. It should be noted that since radial decrease in unit concentration occurs more smoothly than $1/r^2$, most units are located on the periphery of the star, so that the average concentration $\bar{c}_{x0}$ differs from $c_{x,\min} = c_{x0}(r = R_{x0})$ only in a numerical factor close to unity. Hence, the properties of the star (*Table 1*) are determined by its peripheral part. This fact was used in ref. 1 in the construction of the diagram of state of an isolated star (*Figure 2*, *Table 1*). Regions I_x of the diagram correspond to the state of the outer part of the star macromolecule (for further details see ref. 1).

(4) The stretching of branches is at a maximum in the star nucleus and decreases with distance from the centre to the periphery, just as unit concentration.

RESULTS

Star overlapping in solution; threshold concentrations

Let us consider a solution of star-branched macromolecules at volume concentration c. Before carrying out a detailed analysis, a simplified picture will be considered in which an isolated star is characterized by average concentration $\bar{c}_{x0}$ (*Table 1*). The concentration at the threshold of star overlapping is determined from the condition $c^*_x = \bar{c}_{x0}$

$$c^*_x \simeq \begin{cases} n^{-4/5}(\tau p)^{-3/5}f^{2/5} & x = +,\mathrm{mf} \\ n^{-1/2}p^{-3/8}f^{1/4} & x = \Theta \\ n^{-1/2}fp^{-3/2} & x = \mathrm{G} \end{cases} \tag{6}$$

where x characterizes the region of the diagram for an isolated star and the state I_d is not considered.

When the stars overlap, their swelling should decrease, and the size of the star, i.e. the size of star branches, should approach that of similar linear chains in a semidilute solution[6-9]

$$R_x(c) \simeq \begin{cases} n^{1/2}(\tau p c^{-1})^{1/8} & x = + \\ n^{1/2}p^{1/2} & x = \mathrm{mf},\Theta,\mathrm{G} \end{cases} \tag{7}$$

In order to evaluate the threshold concentration c^{**}_x of transition to the regime of a semidilute solution of linear chains (regime II in symbols used in ref. 9), it will be taken into account that at $c > c^*_x$ the intramolecular concentration of the units of a star cannot exceed the solution concentration. Hence at $c > c^{**}_x$

$$\frac{nf}{R^3_x(c)} \leqslant c \tag{8}$$

to give

$$c^{**}_x \geqslant \begin{cases} n^{-4/5}(\tau p)^{-3/5}f^{8/5} & x = + \\ n^{-1/2}p^{-3/2}f & x = \mathrm{mf},\Theta \end{cases} \tag{9}$$

Comparison of (6) and (9) shows that the values of c^*_x and c^{**}_x ($x = +,\mathrm{mf},\Theta$) differ markedly. This difference implies that an additional regime $c^*_x < c < c^{**}_x$ (subsequently referred to as III) exists in the diagram of state of the star solution. In this regime the stars are not isolated, $c > c^*_x$, but retain the memory of their topology so that the size of branches in stars R is greater than that of similar linear chains in a semidilute solution. By analogy with (8), the evaluation of star size may be written as

$$R \geqslant \left(\frac{nf}{c}\right)^{1/3} > R_x(c) \tag{10}$$

where $R_x(c)$ is determined by (7).

In order to check the conclusions of the simplified consideration and to carry out further analysis of star conformations and solution structure, it is necessary to take into account the radial distribution of density in a star (*Table 1*).

Semidilute star solution, region III

Let us consider a solution of stars at a concentration c higher than the threshold concentration c^*_x ($x = +,\mathrm{mf},\Theta$) (equation (6)). According to ref. 2 and the general picture of semidilute polymer solutions[6-9], it will be assumed that the denser inner star parts at a concentration $c_{x0}(r) > c$ are not affected by the perturbing action of other stars, which is spread only to the outer star parts at a concentration $c_{x0}(r) < c$.

The density profile with respect to the centre of the particular star is given by

$$c(r)\simeq\begin{cases} c_{x0}(r) & r<\rho_x \\ c & \rho_x<r<R_x \end{cases} \tag{11}$$

where R_x is the overall size of the star in a semidilute solution and ρ_x is the radius of its inner unperturbed part determined from the condition

$$c_{x0}(r=\rho_x)=c \tag{12}$$

In subsequent discussion the inner part of the star will be called a core in order to distinguish it from the star nucleus of radius r_d and it will be assumed that $\rho_x>r_d$.

Equations (6) and (12) and the data in *Table 1* are used for the determination of the radius of the unperturbed part of the star

$$\rho_x\simeq\begin{cases} c^{-3/4}f^{1/2}(\tau p)^{-1/4}\simeq R_{x0}\left(\dfrac{c_x^*}{c}\right)^{3/4} & x=+,mf \\ c^{-1}f^{1/2}p^{-1/4}\simeq R_{x0}\dfrac{c_x^*}{c} & x=\Theta \end{cases} \tag{13}$$

and the fraction of its units in this part

$$v_x\simeq\begin{cases} c^{-5/4}f^{1/2}(\tau p)^{-3/4}n^{-1}\simeq(c_x^*/c)^{5/4} & x=+,\mathrm{mf} \\ c^{-2}f^{1/2}p^{-3/4}n^{-1}\simeq(c_x^*/c)^2 & x=\Theta \end{cases} \tag{14}$$

Other $nf(1-v_x)$ units of the given star are located in the spherical layer $\rho_x<r<R_x$, which can also contain similar units of other neighbouring stars. Let the units of the given star constitute the fraction $\mu_x\leqslant 1$ of all the units in this spherical layer. The overall size of the star R_x is determined by the obvious condition

$$R_x^3-\rho_x^3\simeq\frac{fn(1-v_x)}{c\mu_x} \tag{15}$$

(numerical coefficients have been omitted, as before).

In order to simplify subsequent analysis, it will be assumed that $c\gg c_x^*$. Then we have $v_x\ll 1$, $\rho_x\ll R_x$ and

$$R_x\simeq k_x\left(\frac{fn}{c}\right)^{1/3}\simeq k_xR_{x0}\left(\frac{c_x^*}{c}\right)^{1/3} \qquad x=+,\mathrm{mf},\Theta \tag{16}$$

$$\frac{\rho_x}{R_x}\simeq\begin{cases} k_x^{-1}(c_x^*/c)^{5/12} & x=+,\mathrm{mf} \\ k_x^{-1}(c_x^*/c)^{2/3} & x=\Theta \end{cases} \tag{17}$$

where the value of $k_x=\mu_x^{-1/3}\geqslant 1$ requires further evaluation.

It should be noted, however, that apart from the dependence on this evaluation, it follows from (16), which is in complete correlation with (10), that at $c_x^*<c<c_x^{**}$ ($x=+,\mathrm{mf},\Theta$) regime III exists in which the outer star parts remain extended. In fact, let us consider (16) for the case of the minimum star size, i.e. at $\mu_x=k_x=1$. Non-extended chains (branches) consisting of $n(1-v_x)\approx n$ monomers in a semidilute solution at a concentration c are characterized by the size $R_x(c)$ according to (7). Equations (7) and (16) give the degree of branch stretching

$$\frac{R_x^2}{R_x^2(c)}\simeq\begin{cases} \left(\dfrac{c_x^{**}}{c}\right)^{5/12} & x=+ \\ \left(\dfrac{c_x^{**}}{c}\right)^{2/3} & x=\mathrm{mf},\Theta \end{cases} \tag{18}$$

where c_x^{**} is determined by the sign of equality in (9).

Now let us consider the possible values of μ_x and k_x in regime III. The case $\mu_x=k_x=1$ corresponds to complete mutual impermeability of stars behaving as quasiglobular particles[12]

$$R\simeq\left(\frac{fn}{c}\right)^{1/3} \tag{19}$$

In the concentration range considered here, the star solution is a densely packed system of segregated stars. Mutual impenetrability and dense packing of stars lead to the existence of at least short-range order in star arrangement

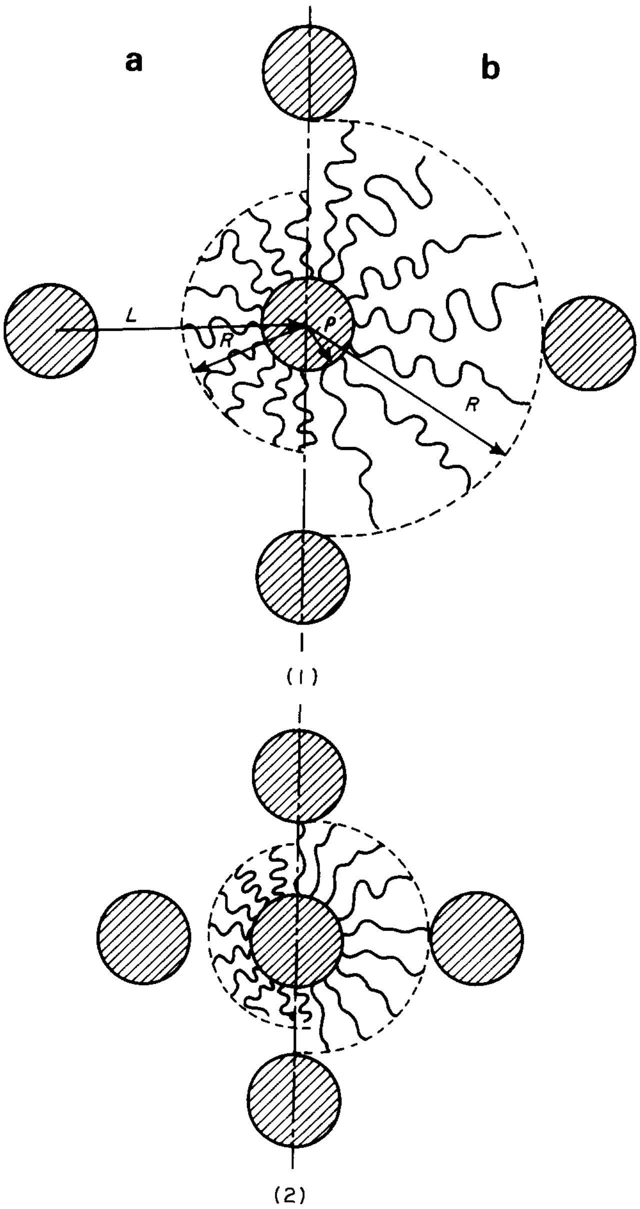

Figure 3 Scheme for the state of semidilute solution of stars in regime III, at two concentrations $C(1)<C(2)$: (a) complete star segregation, $R=L/2$; (b) overlapping of outer star parts, $R=L$, $k_x=2$. The spheres are star cores, outer parts of branches are shown only for the middle star

This situation is on the whole also retained with the assumption that the outer parts of the stars can overlap ($\mu_x<1$, $k_x>1$) because they contain non-overlapping cores with grafted radially extended chains.

Figure 3 shows the scheme for the structure of solution at two concentrations. Case (a) corresponds to the assumption of complete impermeability of stars, $\mu_x=k_x=1$, and case (b) corresponds to the overlapping of the outer parts of stars with the maintenance of the short-range order.

Diagram of state of star solution

Figure 4 shows the temperature–concentration diagrams for solutions of star-branched macromolecules with flexible, $p=1$ (*Figures 4a* and *4d*), and stiff, $p>1$ (*Figures 4b* and *4c*), branches at different numbers of branches: $p^{3/2}<f<n^{1/2}p^{-3/2}$ (*Figures 4a* and *4b*), $1<f<p^{3/2}$ (*Figure 4c*) and $f>n^{1/2}$ (*Figure 4d*). The diagrams contain the regions I_x, II_x and III at $x=+$, mf and Θ (and in the case $f<p^{3/2}$ they also contain additional Gaussian regions I_G and II_G). Equations of boundaries between the regions are listed in *Table 2* and the sizes of stars are given in *Table 3*.

Regions I_x ($x=+$,mf,Θ,G) correspond to dilute solutions containing isolated stars (see *Figure 2* and Introduction).

Regions II_x ($x=+$,mf,Θ,G) are usual regions of semidilute solutions of linear chains in which each branch

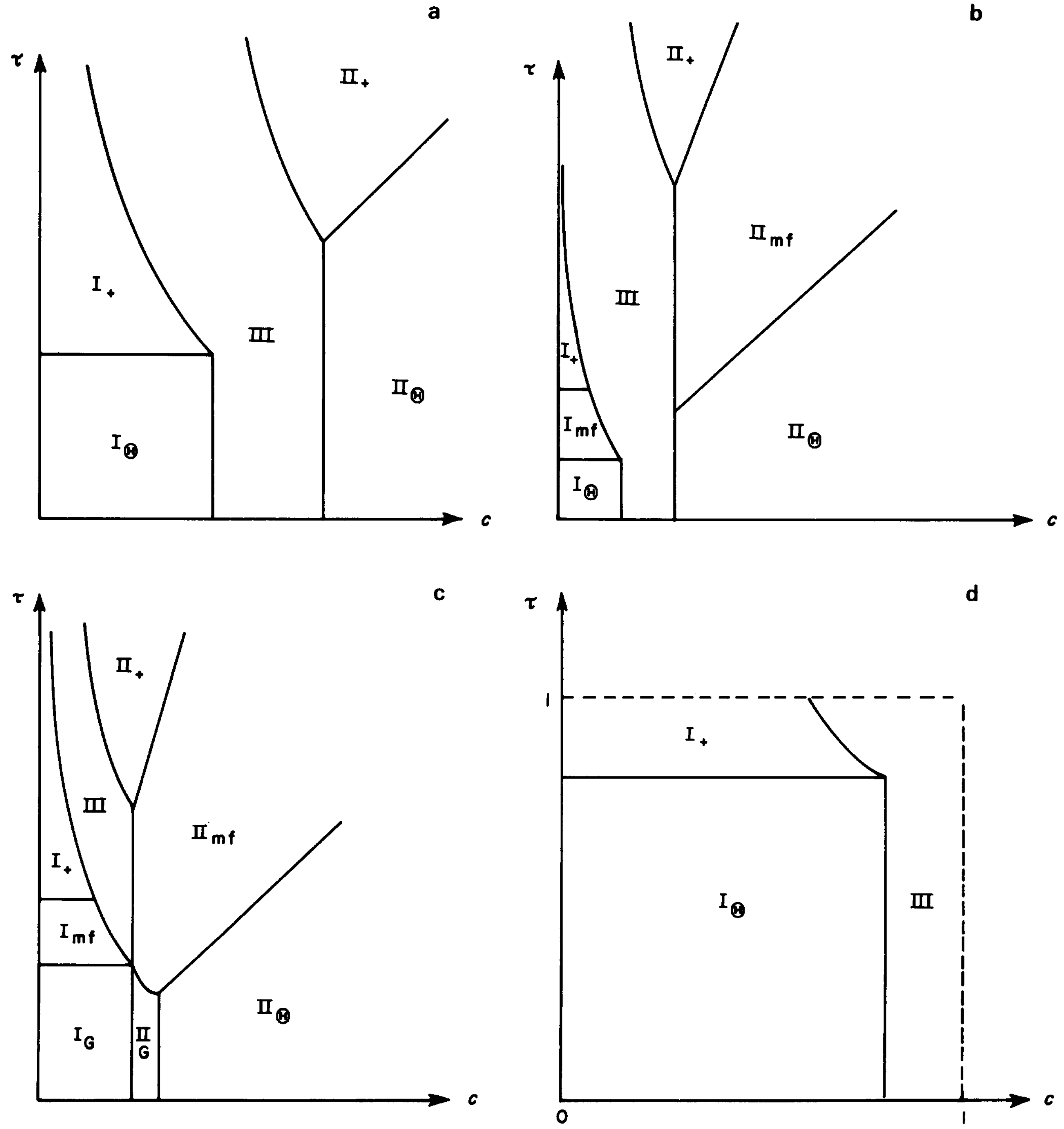

Figure 4 Temperature–concentration diagrams of solutions of star-branched macromolecules with flexible, $p=1$ (*4a* and *4d*), and stiff, $p>1$ (*4b* and *4c*), branches with different branch numbers: $p^{3/2}<f<n^{1/2}p^{-3/2}$ (*4a* and *4b*); $f<p^{3/2}$ (*4c*); $f>n^{1/2}$ (*4d*)

Table 2 The boundaries between the regions in the (τ–c) diagram (*Figure 4*); $c' = cn^{1/2}$, $\tau' = \tau n^{1/2}$

I_{Θ}–I_{mf}	I_{mf}–I_{+}	$I_{+,mf}$–III
$\tau' \sim f^{1/4}p^{-3/8}$	$\tau' \sim f^{1/4}p^{3/2}$	$c' \sim (\tau' p)^{-3/5} f^{2/5}$
I_{Θ}–III	III–$II_{\Theta,mf}$	III–II_{+}
$c' \sim f^{1/4}p^{-3/8}$	$c' \sim fp^{-3/2}$	$c' \sim (\tau' p)^{-3/5} f^{8/5}$
II_{+}–II_{mf}	II_{mf}–II_{Θ}	I_{mf}–I_{G}
$\tau' \sim c' p^{3}$	$\tau' \sim c'$	$\tau' \sim p^{3/2} f^{-1}$
I_{G}–II_{G}	II_{G}–II_{mf}	II_{G}–II_{Θ}
$c' \sim fp^{-3/2}$	$c' \sim \tau'^{-1}$	$c' \sim 1$

Table 3 The star sizes and intramolecular concentration

	I_x	III	II_{+}	$II_{\Theta,mf,G}$
R_x	R_{x0}	$(Nc^{-1})^{1/3}$	$N^{1/2} f^{-1/2} (\tau p c^{-1})^{1/8}$	$N^{1/2} f^{-1/2} p^{1/2}$
$\bar{c}_x$	$\bar{c}_{x0}$	c	$N^{-1/2} f^{3/2} (\tau p c^{-1})^{-3/8}$	$N^{-1/2} f^{3/2} p^{-3/2}$

behaves as an individual polymer chain in the corresponding regime[6,9]. They differ from the semidilute solutions of linear chains because of the retention of central denser star cores. This difference does not affect the properties of individual branches and the thermodynamics of the solution as a whole (when the part of units in the cores is small).

Region III is the region of the quasiglobular state of stars characterized by a universal dependence of star size on the number of units $N = nf$ and solution concentration c (with the assumption that k_x = constant). Region III separates states I_x and II_x at $x = +,\mathrm{mf},\Theta$. The only exception is the case of the Gaussian state I_G when star swelling is absent both in region I_G and in regions II_G, II_{Θ} and II_{mf} neighbouring on the side of high concentrations.

Figure 5 shows the diagram of state in (f,c) coordinates at τ, N = constant (only the case of flexible chains, $p = 1$, is considered). It is clear that the increase in the degree of branching f of the macromolecule at a fixed degree of polymerization leads to increase in the overlapping concentration c^* and to the appearance and broadening of region III of the phase diagram. At high f values region III exists up to the maximum concentrations attainable (*Figure 4d*).

Blob picture of a star solution in different regions

Figure 6 shows the blob pictures of a star solution constructed for the case of flexible stars, $p = 1$.

Figure 6a(I) shows the blob picture of an individual star (region I). The nucleus of radius r_d consisting of greatly extended chains is located in the centre and surrounded by spherical layers of growing blobs. Each branch is a radially oriented system of blobs in the absence of tangential order, i.e. the branch is located in the cone with a tangentially bent axis.

Figure 6b(I) shows a system of blobs belonging to one branch in its cone with the solid angle $4\pi f^{-1}$ and with a straightened axis (for greater details see ref. 1).

Figure 6a(III) shows the blob picture of a solution in region III. The core of the star retains the same structure with a nucleus in the centre and a system of growing blobs with radius $r_d < r < \rho_x$. The outer part of the star contains blobs of the same size $\xi_x(c)$ determined[1,9] by the solution concentration c

$$\xi_x(c) \simeq \begin{cases} (\tau p)^{-1/4} c^{-3/4} & x = + \\ \tau^{-1/2} p^{1/2} c^{-1/2} & x = \mathrm{mf} \\ p^{1/2} c^{-1} & x = \Theta \end{cases} \tag{20}$$

The number of units in a blob is given by

$$n_{\beta,x} \simeq \begin{cases} (\tau p)^{-3/4} c^{-5/4} & x = + \\ (\tau c)^{-1} & x = \mathrm{mf} \\ c^{-2} & x = \Theta \end{cases} \tag{21}$$

In contrast to the usual semidilute solution, the blob sequence is not random for each branch. This fact is illustrated in *Figure 6b*(III), where one branch is shown in its cone with straightened axis. The inner part of the cone is occupied by the branch part belonging to the star core. The number of outer blobs of the given branch located in the external part, i.e. in the truncated cone, is $n(1 - v_x)/n_{\beta,x}$. Moreover, the branch may occupy either all the blobs of its cone nearest the centre or only a part of them, leaving the others to the branches of neighbouring stars. The

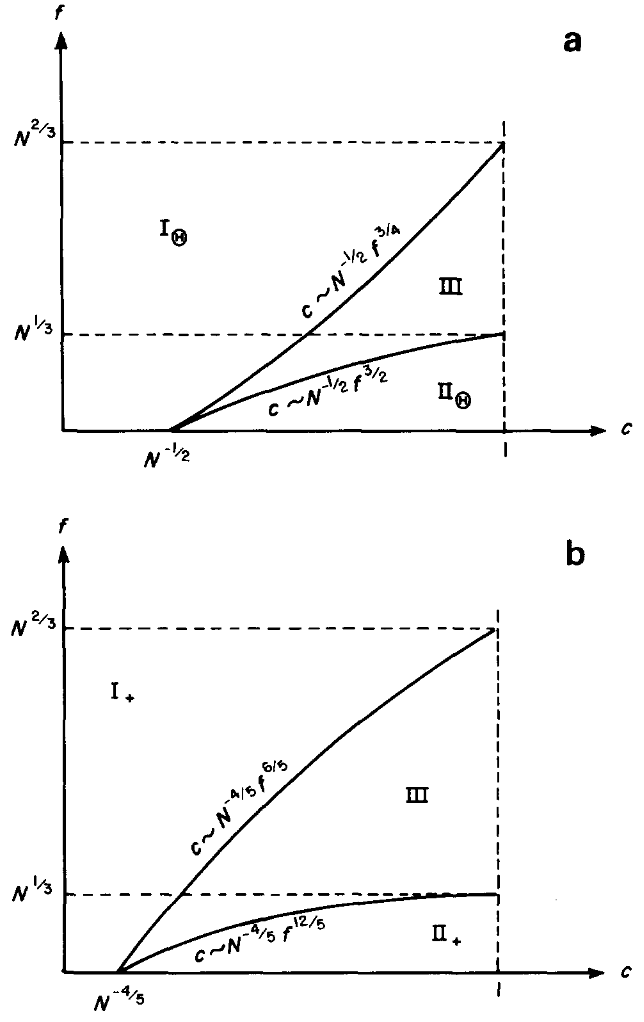

Figure 5 Diagram of state of a solution of flexible-chain stars ($p = 1$) in (f,c) coordinates at τ, N = constant at $\tau = 0$ (*5a*) and $\tau = 1$ (*5b*)

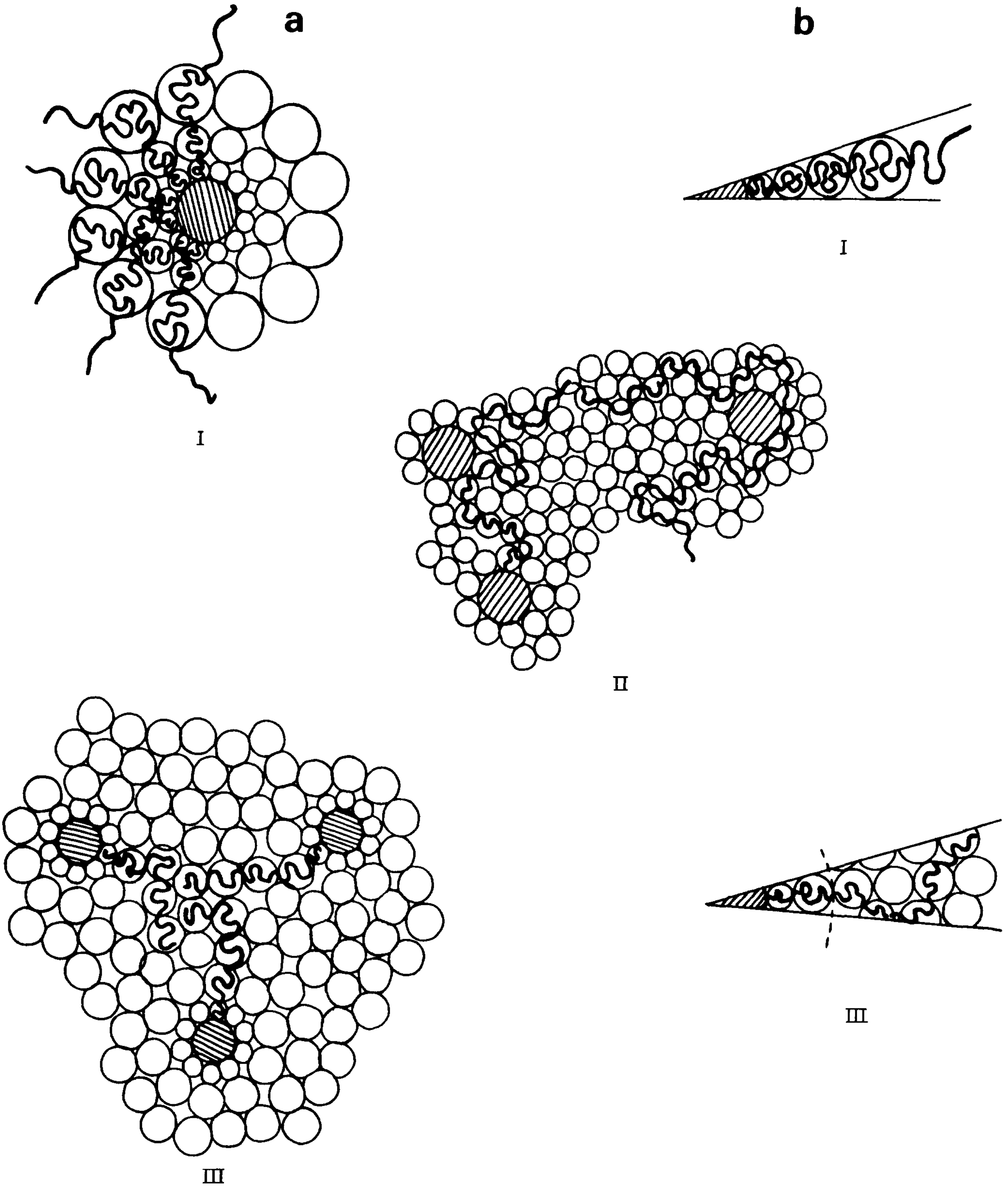

Figure 6 (a) Blob picture of solution and (b) system of blobs of a single branch in its cone with straightened axis in regimes I, II and III. The case of flexible-chain stars, $p = 1$

minimum value of the size of the filled part of the cone corresponds to a dense packing of their blobs

$$R_x \simeq \xi_x \left(\frac{fn}{n_{\beta,x}}\right)^{1/3} \qquad (22)$$

(cf. equation (16)). Comparison of this value with the size of a random coil consisting of blobs (cf. equation (7))

$$R_x(c) \simeq \left(\frac{n}{n_{\beta,x}}\right)^{1/2} \xi_x \qquad 23)$$

clearly shows that in accordance with the previously obtained result we have $R_x > R_x(c)$, at $c_x^* < c < c_x^{**}$, i.e. not only the inner but also the outer parts of stars remain extended in the radial direction. The system of both inner and outer blobs in region III retains radial orientation.

Figure 6a(II) shows the blob picture in regions II. In this case the orientational order and branch extension are retained only in the star cores. The outer parts of branches are usual random coils of blobs; the grafting to the star core does not in the least affect their properties.

The behaviour of the solution of flexible-chain stars shown in *Figure 6* is on the whole independent of solvent strength. The value of τ, however, affects the conformations of chain parts in the outer blobs (and in the blobs located at the periphery of the core) swollen under conditions of a good solvent and the Gaussian blobs in the Θ-region. With increasing solution concentration, the size of these blobs decreases and the range of τ values corresponding to the Θ-region increases correspondingly (cf. ref. 1).

DISCUSSION

Main result and comparison with other theroetical papers

The main result of the present paper is the diagram of state of the star solution (*Figures 4* and *5*) containing three types of regimes: I_x, isolated stars in a dilute solution; III, impermeable (or almost impermeable) stars in a semidilute solution; and II_x, a semidilute solution of star branches.

This diagram is based on the results of scaling analysis[1,2] according to which the branches of an individual star in regimes I_x (apart from regime I_G for stiff-chain stars) are always extended. The general structure of the diagram with three types of regime and the blob picture of the solution in these regimes (*Figure 6*) is determined by inequality (4) rather than by the specific values of exponents β_x and γ_x for individual stars (equations (1) and (2)). It should be noted that in the diagrams in *Figures 4a–c* it was assumed that the core of the star decreasing with concentration nevertheless remains larger than its nucleus up to concentrations $c > c_x^{**}$ corresponding to the boundary between regimes III and II_x. If this condition is not obeyed, the boundary of III and II_x is displaced towards higher c and is unattainable. However, the main feature of the diagram is retained: the transition from regimes I_x ($x = +$,mf,Θ) to regime III rather than to region II_x (with increasing solution concentration, *Figure 4c*).

The diagram of state of a star solution has previously[2] been constructed on the basis of the blob picture of solution. Daoud and Cotton[2], however, have not considered regime III, *assuming* that regimes I_x are in direct contact with regimes II_x in which the outer chain parts are a random coil of blobs. They have not paid attention to the fact that this assumption leads to a contradiction: as has been shown above, the concentrations of the stars' own units in their external layers becomes higher than that of the solution.

In this connection it should be noted, that the scaling concepts[13] widely used recently for the construction of the diagrams of state of various polymer systems always require an independent and careful analysis of the number and type of possible regions of state. If any of these regions is omitted, as in ref. 2, the non-existent boundary between regimes is thus postulated and inadequate conditions of the crossover of physical values at this boundary are established. This automatically leads to erroneous power dependences, at least in one of the regions artifically introduced into contact (see, e.g. ref. 14 and the discussion in ref. 9).

In particular, in ref. 2, the error in the expression for the size of the outer part of the star at $c > c_x^*$ also leads to an erroneous conclusion about the existence of an additional threshold concentration c_{1x}, such that at $c_x^* < c < c_{1x}$ the star size is determined by its core, whereas at $c > c_{1x}$ it is determined by its outer part. As a matter of fact c_{1x} differs from c_x^* only in the numerical coefficient, i.e. it coincides with c_x^* in the approximation used. Hence it was possible to take into account only the properties of outer star parts.

Segregation of stars in regime III

As has been shown in the earlier results section 'Semidilute star solution, region III', in regime III complete or partial star segregation should be observed. Complete segregation leads to smaller losses in the elastic free energies, equation (18). On the other hand, the entropy factor favours the interpenetration of branches of neighbouring stars.

The complete solution of the problem of degree of star segregation and the determination of the coefficient k_x (in equations (16) and (17)) are outside the scope of this paper. Our tentative evaluations show that complete segregation is more advantageous thermodynamically because of the lower degree of branch stretching. A similar conclusion may be drawn from a more detailed analysis carried out by de Gennes[15] for another system: a layer of chains grafted onto a plane and immersed in a solution of similar but mobile chains.

Effects of the segregation of macromolecules have also been considered for the semidilute chain solutions in limited volumes[16,17] in which the properties of the system (existence of restrictions) lead to chain stretching, whereas segregation favours the minimization of this stretching.

As already indicated, completely segregated stars in region III are quasiglobular particles with a denser core and an outer part with a constant density determined by solution concentration (equations (16), (17) and (19)). This also remains true for partial overlapping of the outer star parts when the degree of overlapping k_x depends neither on the star characteristics f and n nor on the solution concentration c.

Stars and block copolymers

It is of interest to point out the analogy between the solutions of macromolecular stars investigated in this paper and the micellar solutions and superstructures of block copolymers. The difference between those systems consists of the fact that in our case the structural element is a star with a given chemical structure (fixed number of branches f). For block copolymers the structural element itself (for example, a micelle) is formed from linear chains of the same type as a result of effective attraction due to poor solubility and/or to the incompatibility of components. Hence, the number of chains f in a spherical micelle equivalent to that of star branches is determined by the characteristics of the block copolymer. Comparison of results of refs. 1, 5 and 18 shows that the individual star behaves just as the individual spherical micelle (dilute solution of stars or micelles) of a two-block copolymer containing a soluble and a shorter insoluble block (region III in ref. 18). In particular, the relationships given in *Table 1* are obeyed for both systems.

When concentration increases, these block copolymers form a regular structure. The shorter blocks form a part of spherical domains, whereas soluble blocks form a matrix containing a certain amount of the solvent. Common features of this superstructure[5,19] and of a star solution in regime III are the presence of an impermeable core, the retention of radial extension of chains grafted onto the cores, partial or complete segregation of chains belonging to different domains (stars) and the existence of at least short-range order in the arrangement of domains (stars).

As a result of the possibility of a change in the chain number in domains of the block copolymers with increasing concentration of the polymer, regime III is stable even in complete absence of solvent (cf. ref. 19), whereas the star system passes into regime II_x with increasing concentration.

NOTE ADDED IN PROOF

Recently we have received two Preprints by T. A. Witten, P. A. Pincus and M. E. Cates, and by T. A. Witten and P. A. Pincus, where the authors, by using the results of ref. 2, considered the concentration dependence of osmotic pressure $\pi(c)$ for a solution of flexible ($p = I$) stars. It has been shown in the preprints that at overlap concentration c^* there is no crossover between ideal gas law $\mathrm{d}\pi/\mathrm{d}c \simeq \pi/c \simeq (nf)^{-I}$ for dilute solution and the dependence $\mathrm{d}\pi/\mathrm{d}c \simeq \pi/c \simeq c^{5/4}$ for semidilute solution (in good solvent). A rapid change in $\pi(c)$ (in $f^{3/2}$ times) near c^* permits the authors to come to the conclusion that at c^* the star's solution should crystallize into an 'ordered steric colloidal crystal'.

This conclusion is in complete agreement with the results of our paper, where the structure of star-branched macromolecule solution in the quasiglobular regime III (which separates regimes of dilute (I_x) and semidilute (II_x) solution) is investigated.

As an analysis shows, despite the difference between the structure of solution in regime III and in semidilute regimes II_x, thermodynamically, regime III consists of regimes III_x, the scaling concentration dependences $\pi(c)$ in which coincide with those of regime II_x, i.e. $\pi_+ = (\tau p)^{3/4} c^{9/4}$, $\pi_{\mathrm{mf}} = \tau c^2$, $\pi_\theta = c^3$. So the conclusion about the singularity in the concentration dependence $\pi(c)$ near c^* is confirmed by the results of our paper. Note that the origin of this singularity near the overlap concentration c^* is the mutual impermeability and segregation of stars near the boundary c^* of the I_x regime and in the whole regime III_x. A similar effect has been noticed by Daoud and de Gennes[16] for a system of chains trapped in a capillary.

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