Concept of quasimonomers and its application to some problems of polymer statistics

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The concept of quasimonomers is introduced, i.e. the concept of disconnected quasiparticles, which can be effectively substituted for a chain of connected monomers in the analysis of volume interactions in polymeric coils. Such a substitution becomes possible because each monomer of an infinite homogeneous chain is 'standardly surrounded' by the other monomers (primarily by near neighbours along the chain) and solvent molecules. This 'standard surrounding' renormalizes the monomer characteristics in such a way that each monomer can be considered as a disconnected quasiparticle, the properties of which do not coincide with the properties of the initial monomer. The application of the concept of quasimonomers to the analysis of volume interactions in inhomogeneous macromolecules (finite linear macromolecules, macromolecules with defects and branched macromolecules) leads to results which differ from the results of classical Flory-type theories. This is connected with the fact that the interaction characteristics for these macromolecules turn out to be dependent on the positions of corresponding monomers in the chain. The following topics are considered with the help of the method of quasimonomers: the θ behaviour of finite chains, of chains with defects and of branched chains; the partial specific volume of polymeric macromolecules; and the relation between the polymer chain models. In Appendix 2 the good solvent behaviour of branched macromolecules is also discussed.

INTRODUCTION

The Flory–Huggins theory[1] is now the most widely used theory of polymer solutions. However, it has some shortcomings and among them is the fact that the monomer–monomer volume interactions are described by the single parameter χ, which is independent of the polymer concentration in the solution and of the position of interacting monomers in the chain. This shortcoming was partly eliminated in the so-called 'new' Flory theory (see, for example, ref 2); in this theory the parameter χ depends on concentration.

At the same time, as far as the author knows, the dependence of the parameters characterizing the monomer–monomer volume interactions (such as χ*) on the position of interacting monomers in the chain has not hitherto been considered. It will be shown below that this dependence exists and is important in the theory of dilute polymer solutions. In order to study this dependence it is useful to introduce a picture of the polymeric coil as a low density cloud of special quasiparticles–quasimonomers.

In this work we first formulate the concept of quasimonomers and, using this concept, we consider the dependence of monomer–monomer interaction parameters on the position of monomers in the chain. We then consider the physical problems of polymer statistics, which can be solved with the help of this concept.

Throughout this paper we shall deal with dilute polymer solutions (i.e. with the isolated macromolecule surrounded by the solvent), because it is for these solutions that the effects under consideration are most important.

The results obtained are not dependent on the choice of the specific model of the polymer chain. However, in order to be precise we shall always imply the model of 'interacting beads on a flexible immaterial filament' (*Figure 1*). The problem of correlation of the results obtained for this model with the results for other models of the polymer chain will be considered below.

The concept of quasimonomers will be introduced in a

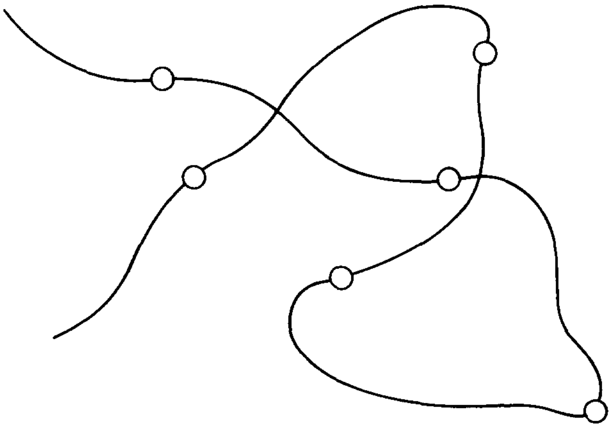

Figure 1 Model of beads: the polymeric chain is represented as a long flexible immaterial filament, on which interacting beads are strung

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* In order to characterize the monomer–monomer interaction we shall use the virial coefficients B, C . . . (more exactly, the virial coefficients of the interaction of quasimonomers, see below) instead of χ

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purely qualitative, intuitive way. The corresponding mathematical foundation can be found in ref 3.

CONCEPT OF QUASIMONOMERS

It is well-known that at large degrees of polymerization (N) the average density of monomers in the volume of the coil is low and tends to zero when $N \to \infty$. We first suppose that in order to calculate the free energy of mixing of monomers with the solvent we can imagine that the polymeric coil is a cloud of disconnected monomers (this picture is used, for example, in the Flory theory). Then at large N this cloud will be very dilute. This implies that the number of binary interactions of monomers in the cloud (which are described by the second virial coefficient, B) prevails over the number of interactions of higher order (which are described by the third and fourth virial coefficients, $C, D \ldots$ etc) so these latter interactions can be neglected with high degree of accuracy. Thus, the properties of polymeric coils at large N depend only on one parameter B among all the characteristics of monomer–monomer interaction†.

This shows the universality of the behaviour of polymeric coils[4]. The properties of polymeric coils depend in a universal manner on the second virial coefficient, B, independent of the specific character of the forces forming this virial coefficient.

However, the above consideration does not take into account the fact that the monomers are not distributed independently in the 'cloud', but are connected in the chain. Thus, in spite of the low value of the *average* monomer density in the coil at large N, the *local* density of other monomers near the given monomer is generally not low and does not decrease when $N \to \infty$[5]. This high local density is caused by monomers which are close to the given monomer along the chain. The second virial coefficient is insufficient to describe the case of high density and thus the above formulation of the universality concept is not valid.

However, it is intuitively clear that the low value of the average monomer density in the coil must lead to some kind of universality. In practice, this turns out to be so[3]. This universality can be explained as follows. Let us consider the interactions in the polymeric coil of the remote *parts* of the chain instead of the interactions of the monomers themselves. The small value of the average density in the coil implies that the binary interactions of the parts of the chain prevail over their higher order interactions. Analogous to the above consideration, such a dominance of binary interactions must lead to universality, but this universality must be expressed in terms of the universal dependence on some effective renormalized second virial coefficient of the interaction between the parts of the chain B^* (instead of B).

We have seen that this kind of universality is connected with the picture of the polymeric coil as a cloud of disconnected particles. Thus, we suppose (for the more strict treatment see ref 3) that in order to consider the effect of monomer–monomer interactions, the polymeric coil can be represented as a cloud of N disconnected particles – quasimonomers. In contrast to monomers, the quasimonomers interact with the renormalized characteristics [virial coefficients $B^*, C^*, D^* \ldots = f(B, C, D \ldots)$, instead of $B, C, D \ldots$], which effectively take into account the chain connectivity. The character of the relationship $B^* = B^*(B, C, D \ldots)$ is considered in detail in ref 3. Each quasimonomer is based on its bare monomer; the quasimonomer appears as a result of the renormalization of the interactions of bare monomer due to the presence of neighbouring chain monomers. Roughly speaking, these monomers 'interfere' in the interactions of the bare monomer and renormalize them.

Quasimonomers are similar to quasiparticles, which are well-known in condensed matter physics in the sense that they represent the collective properties of all the monomers of the chain. Each monomer contributes to the characteristics of each quasimonomer. In fact, each monomer can 'interfere' in the interactions of the bare monomer of each quasimonomer.

However, the probability of such an 'interference' differs depending on i, the number of monomers along the chain between the monomer under consideration and the bare monomer. In order to 'interfere' the given monomer must approach the bare monomer, i.e. the section of the chain between these two monomers must form a loop. If this section of the chain is not perturbed by volume interactions, the probability of loop formation depends on i as $i^{-3/2}$ (at large enough i). Thus the contribution of a given monomer to the characteristics of a given quasimonomer decreases when i increases as $i^{-3/2}$ ‡.

It is easy to see that the cloud of N disconnected monomers localized in the volume of a polymeric coil, is very dilute at large N. Thus it is sufficient to take into account only binary interactions of quasimonomers (coefficient B^*); interactions of higher order can be considered as small corrections in this case.

THE MODEL

Before proceeding to the applications of the concept of quasimonomers to some problems of the statistical physics of polymer solutions it is necessary to define the polymer chain model more exactly. It has already been mentioned in the Introduction that we shall consider the model of 'interacting beads on a flexible immaterial filament' (see *Figure 1*). We shall assume that the chain of beads is gaussian, i.e. that the conditioned probability that the $(j + 1)$th bead is situated at $\vec{x}_{j+1}$, provided that the jth bead is situated at $\vec{x}_j$, is equal to:

$$g(\vec{x}_{j+1} - \vec{x}_j) = \left(\frac{3}{2\pi a^2}\right)^{3/2} \exp[-3(\vec{x}_{j+1} - \vec{x}_j)^2/2a^2] \quad (1)$$

It can be seen that the value of a in equation (1) is the average spatial distance between two subsequent monomers along the chain.

We shall assume further that the beads (or monomers) interact with the usual potential of the type shown in *Figure 2*. At small distances monomers repel each other due to their hard cores; at larger distances the interaction has an attractive character. We shall consider only short range forces of monomer–monomer interaction. We denote the radius of interaction as r_0 and the corresponding volume $v \sim r_0^3$.

The question naturally arises as to whether the results obtained for the rather artificial model described can be applied to real polymer chains. This question is considered in Appendix 1 where it is shown that each polymer chain can be related to an equivalent chain of beads with correlations given by equation (1) in such a way that all the macroscopic

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† χ, which is used in the Flory theory instead of B, is related to B.

‡ If the section of the chain forming the loop expands with coefficient α due to volume interactions, then this dependence is modified as $\alpha^{-3}\, i^{-3/2}$

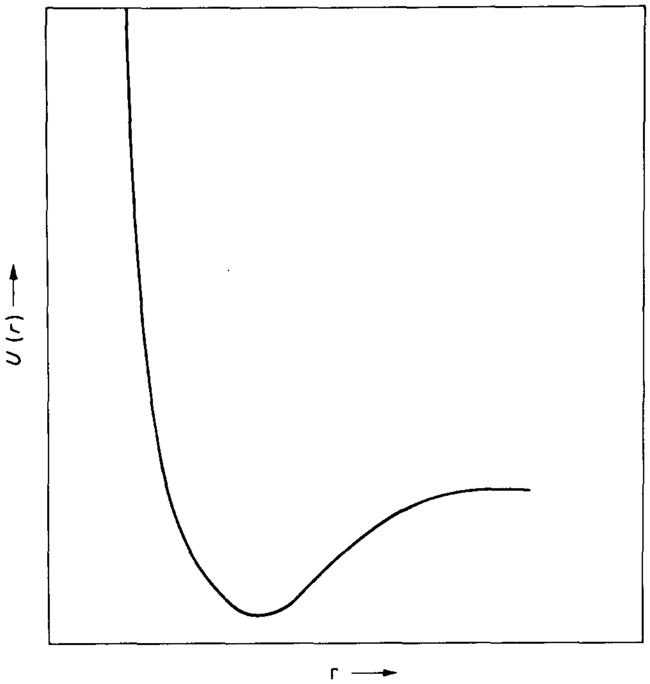

Figure 2 Typical potential $U(r)$ for the interaction of beads; r is the distance between the beads

conformational characteristics of two corresponding coils will coincide. Thus the fact that we shall consider this model throughout does not lead to a loss of generality: it is easy to reformulate the results for any other model by means of relating the equivalent model of beads to it (see Appendix 1).

In particular, in Appendix 1 it is shown that for flexible polymer chains with the usual interactions between the parts of the chain, the parameters $\nu \sim r_0^3$ and a^3 of the equivalent model of beads are of the same order of magnitude $\nu \sim a^3$ (*Figure 3a*). Since we shall deal further only with flexible chain polymers, we shall assume that the relation $\nu \sim a^3$ is valid.

The following fact is also to be noted. B^* is the sum of the contributions from the interaction of bare monomers, which is equal to B, and of the renormalizing contribution due to the 'interference' of other monomers. It is clear, that for flexible chains ($\nu \sim a^3$, *Figure 3a*) this 'interference' is so essential that both contributions are of the same order of magnitude. Thus, on the one hand, the behaviour of B^* is qualitatively similar to the behaviour of B, i.e. B^* is of order ν at high temperatures and becomes zero at some lower temperature; on the other hand, B^* differs essentially from $B\,[(B^* - B)/B \sim 1]$. In particular, the Boyle temperature ($B = 0$) differs considerably from the temperature at which $B^* = 0$. At this latter temperature the effect of the monomer–monomer interaction vanishes, and thus we identify this temperature with the Flory's θ point[3,4].

It is thus seen that $B = \nu\tau$ is an estimation which can be used for B^* in the model under consideration, where $\tau = (T - \theta)/T$ is the relative temperature departure from the θ point.

B^* is the sum of the contributions from each monomer along the chain. Taking into account the estimation for B^* and the fact that the contribution $\Delta B^*(i)$ caused by the monomer which is situated i monomers away from the bare monomer varies with i as $i^{-3/2}$, it is easy to show that $\Delta B^*(i) \sim \nu \cdot i^{-3/2}$. If the chain between the bare and the given monomer is perturbed by volume interactions, then $\Delta B^*(i) \sim \nu \cdot i^{-3/2}\alpha^{-3}$.

It is essential that at the θ point only the sum of all $\Delta B^*(i)$ (and not each contribution taken separately) becomes zero. Thus, the dependence on τ is not indicated in the estimation of $\Delta B^*(i)$.

θ BEHAVIOUR OF FINITE CHAINS AND CHAINS WITH DEFECTS

The introduction of quasimonomers does not lead to new effects in comparison with the Flory theory in the case of infinite and homogeneous polymer chains since in this case B is simply replaced by B^* in all the Flory expressions. However, real polymer chains are always inhomogeneous; even if the chain is linear and has no structural defects, it is always finite. The new effects connected with the concept of quasimonomers (the dependence of B^* on the position of interacting monomers in the chain) become apparent only for inhomogeneous chains.

First of all we shall consider a finite polymer chain consisting of N monomers, or, more specifically, the behaviour of such a chain near the θ point, i.e. near the point, at which $B^* = 0$. This problem has been studied by the author[3]. The corresponding results are obtained from the point of view of the concept of quasimonomers, and, as everywhere in this paper, by means of semiqualitative estimations.

The binary collision of two quasimonomers, i.e. of two parts of the chain, is characterized by the virial coefficient B^* only for an infinite chain. In the case of a finite chain some of the monomers which contribute to B^* for an infinite chain are absent (*Figure 4*); thus the virial coefficient B^* cannot be realized entirely. If the bare monomers of two quasimonomers are situated at a distance of i_1 *and* i_2 monomers respectively from the nearest ends of the chain, it is

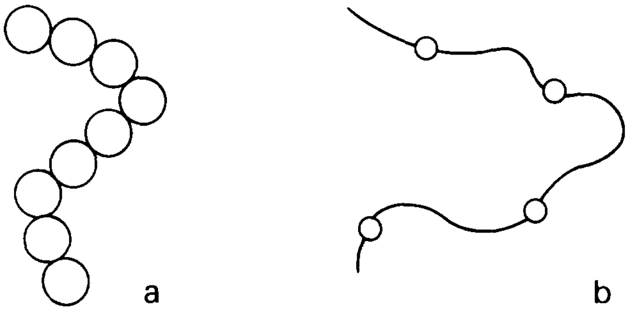

Figure 3 The equivalent models of beads (a) for flexible and (b) for stiff polymer chains

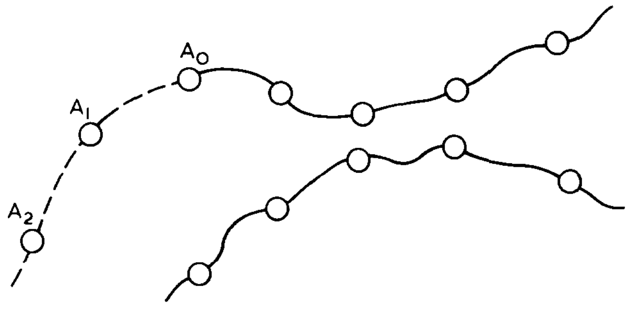

Figure 4 The collision of two parts of the chain. Monomer A_0 is situated at the end of the chain. Due to the absence of monomers A_1, A_2 . . ., which would be present in the case of infinite chain, the virial coefficient B^* cannot be realized entirely

easy to understand (see above and *Figure 4*) that the difference between the virial coefficient of the binary interaction of such quasimonomers and B^* is of order

$$\sim \nu \sum_{j=i_1}^{\infty} j^{-3/2} + \nu \sum_{j=i_2}^{\infty} j^{-3/2} \sim \nu \cdot i_1^{-1/2} + \nu \cdot i_2^{-1/2}$$

or, in other words, this difference is proportional to the difference Δn between the actual local monomer density at the point of collision of bare monomers and the local density, which would occur at this point in the case of an infinite chain.

It can be seen that the second virial coefficient of interaction between two quasimonomers depends on the position of corresponding bare monomers in the finite chain. In terms of the Flory theory this would mean that the parameter χ depends on the position of the interacting monomers in the chain.

The sign of the corrections to B^* near the θ point due to the finite nature of the chain is now discussed. When the usual forces of monomer–monomer interaction are present (*Figure 2*) the second virial coefficient, B, is the first among the virial coefficients to change its sign when the temperature is lowered. This means that since $B^* = B^*(B, C, D \ldots)$, the value of B is negative at the θ point (where $B^* = 0$), because B must effectively compensate in the expression for B^* for the contributions from the other virial coefficients which remain positive when B has become negative. Further, the corrections to B^* due to the finite nature of N are connected with the increase of the role of the interactions of bare monomers in comparison with the renormalizing interactions (some of these latter interactions are not realized near the ends of the chain), i.e. by the increase of the role of B in $B^* = B^*(B, C, D \ldots)$. Since $B < 0$, the corrections to B^* are negative, i.e. they correspond to the effective attraction.

The most simple method of consideration of the θ behaviour of polymeric chains is the perturbation theory (see, for example, ref 6). In order to take our results into account it is necessary to replace the binary cluster integral B by B^* – constant x $(\nu \cdot i_1^{-1/2} + x \cdot i_2^{-1/2})$ in the sums of the perturbation theory[6] where the numerical constant is of the order of unity. From first order perturbation theory we obtain the expansion factor, α, of a polymer chain[3] [§]:

$$\alpha^2 \equiv \frac{\langle R^2 \rangle}{\langle R^2 \rangle_0} = 1 + C_1 \tau N^{1/2} - C_0 \qquad (2)$$

Here $\langle R^2 \rangle$ and $\langle R^2 \rangle_0$ are the mean square end-to-end distances of the chains with and without monomer–monomer volume interactions; C_1 and C_0 are numerical constants of order unity. The estimations $B^* \sim \nu\tau$ and $\nu \sim a^3$ (see above) have already been taken into account in equation (2). The third term in equation (2) appears as a result of the corrections due to the finite nature of N.

First of all, it can be concluded from equation (2) that accounting for the corrections due to the finite nature of the chain is much more essential than accounting for the corrections due to the chain ends, i.e. due to the presence of other sorts of monomers at the ends of the chain. Accounting for the former corrections gives rise to a term ~ 1 in equation (2) whereas accounting for the latter gives rise to a term $\sim N^{-1/2}$.

It is easy to see from equation (2) that $\alpha^2 = 1$ at $\tau = C_0/N^{1/2}C_1 \sim N^{-1/2}$. Thus the temperature θ_α, at which $\alpha^2 = 1$, does not coincide with the true θ temperature (the temperature at which $B^* = 0$) for finite chains: $(\theta_\alpha - \theta)/\theta \sim N^{-1/2}$, $\theta_\alpha > \theta$. Moreover, at the true θ point $\alpha^2 = 1 - C_0 < 1$, i.e. the polymeric coil is contracted, and this contraction can be considerable, because C_0 is of the order of unity.

It may be seen that for every value of the type $\langle R^p \rangle / \langle R^p \rangle_0$ with some $p \neq 2$ we obtain an expression similar to equation (2) but with different numerical coefficients from first order perturbation theory. Thus the temperature at which this value is equal to unity will differ from the true θ temperature, the relative difference being of the same order $\sim N^{-1/2}$, but with a different numerical coefficient (this coefficient will depend on p). The same is true for the temperature at which the osmotic second virial coefficient A_2 becomes zero, θ_{A_2}.

It can be concluded[3] that for finite chains there exists a θ region (and not the θ point) of relative width $\Delta\theta/\theta \sim N^{-1/2}$. The θ region is situated above the true θ temperature. Depending on which property is used for the determination of the θ conditions we obtain different points within the θ region. The true θ point (at which $B^* = 0$) can be determined by means of the extrapolation $N \to \infty$.

We now consider some experimental verifications of the results obtained. It must be noted that the new effects to which the application of the method of quasimonomers leads are rather small for linear finite chains (relative order $N^{-1/2}$). Thus, as far as the author knows, systematic experimental studies of the influence of the method of determination and of the number of monomers in the chain on the θ temperature have not hitherto been carried out. However, the accuracy of computer experiments allows us to deal with these problems and the results obtained in reports of this kind are in agreement with our approach: here we give some examples. It can be seen from the *Figure 11* of ref 8, that the first correction to the value of the fourth reduced moment of the mean square radius of gyration has the relative order $N^{-1/2}$ at the θ point (and not N^{-1}, as supposed by the authors). In ref 9 the θ temperature was determined by the condition $\alpha^2 = 1$ (temperature θ_α) and it was shown (see *Table 2* ref 9) that θ_α decreases when N increases, indicating the effective attraction at the θ point (in the case of the effective repulsion the trend would be the opposite). In ref 10 the dependence of the temperature θ_{A_2} at which $A_2 = 0$ on $N^{-1/2}$ was studied (see *Figure 2*, ref 10). It was shown that at large N this dependence is linear and that θ_{A_2} decreases when N increases. All these facts are in agreement with our results.

In ref 11 the average potential of the interaction of two polymeric coils at the θ point was calculated as a function of the intercoil distance by the Monte Carlo method. It was shown that this potential does not correspond to the ideal gas (as in the Flory theory), but corresponds to attraction at large distances and to repulsion at smaller distances. This is in accord with our result that the parameters describing the interaction of quasimonomers depend on the position of corresponding bare monomers in the chain and thus these

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[§] The three body collisions of the remote parts of the chain (which are described by the coefficient C^*) also give the corrections to the usual expression for the first order perturbation theory[3,7]. These corrections correspond to the effective repulsion at the θ point and apparently play a less important role than those in equation (2) because: (a) they are of order 1/ln N (see ref 3); (b) computer experiments indicate effective attraction at the θ point (see below).

parameters cannot become zero for all the quasimonomers simultaneously. The effect obtained in ref 11 was attributed in ref 12 to the non-local nature of the monomer–monomer interaction. However, the corrections due to the non-local nature are of relative order $1/N$ (see ref 12), whereas the corrections studied above due to the dependence of the interaction parameters on the position of bare monomers in the chain are of relative order $N^{-1/2}$. Thus it is natural to assume that it is these latter corrections which are responsible for the results obtained in ref 11.

Finally, it should be noted that the notion of a θ region was originally introduced in refs 8 and 13, based on the analysis of computer data. However, in these reports it was assumed that the θ region remains finite even when $N \rightarrow \infty$. This result was apparently due to the inexact extrapolation to $N \rightarrow \infty$, which was considered to be linear in the coordinates θ and $1/N$; in fact the extrapolation is linear in the coordinates θ and $N^{-1/2}$.

The θ behaviour of a polymer chain with defects (for example, inclusions of other sorts of monomers) is now considered. A chain with defects is another example of an inhomogeneous chain, and thus the application of the method of quasimonomers to this problem must lead to new effects. The corresponding treatment can be found in ref 3, so we shall not repeat it here. We only note that when the concentration of defects in the chain is large enough, its influence on the θ behaviour can be essential (in contrast to the influence of the finite nature of the chain and is accessible to observation even in rough experiments[14]. A further study in this field will allow us to verify the relations obtained in ref 3.

θ BEHAVIOUR OF BRANCHED MACROMOLECULES

In this section we shall consider the behaviour of comb-branched and star-branched macromolecules in θ solvents. Experimental studies of this problem[15] have revealed considerable deviations from Flory-type theory, which was developed for branched polymers[16]. It was shown that at the θ point for the corresponding linear polymer the expansion factor of the branched macromolecule, α^2, is essentially larger than unity and the osmotic second virial coefficient A_2 is larger than zero, whereas according to the theory[16] we should observe $\alpha^2 = 1$ and $A_2 = 0$ at this point. The temperature θ_{A_2} at which $A_2 = 0$ and the temperature θ_α, at which $\alpha^2 = 1$, are essentially lower than the θ temperature for linear polymers and do not coincide with one another. These deviations are so large that they cannot be explained only by the presence of anomalous groups at the branching points and at the end-points.

The existence of considerable deviations from the Flory theory is not surprising. The structure of comb-branched and star-branched macromolecules is highly inhomogeneous, i.e. it differs essentially from the structure of linear infinite chains, and we have seen that for inhomogeneous chains the Flory approach must be modified with the help of the concept of quasimonomers; this modification is carried out below.

The comb-shaped and star-shaped macromolecules are characterized by the following parameters: N, the total number of monomers in the macromolecule; n, the number of branches; and σ, the ratio of the number of monomers in the branches to the number in the backbone. We shall assume that $N \gg 1$ and $n \gg 1$; σ can take any value from 0 (linear polymer) to ∞ (star-branched polymer).

We saw above that in the case of a finite linear chain, the absence of sections of the chain which are necessary for its homogeneity lead to effective attraction at the θ point. In the case of branched polymers we expect the opposite situation in which the presence of additional sections of the chain (more than necessary for homogeneity) must lead to effective repulsion at the θ point*). This effective repulsion is due to the 'extra interference' in the interaction of bare monomers, additional to the 'normal interference', which would exist in the case of a linear infinite chain. By analogy with the above section we can say that this 'extra interference' leads to a second virial coefficient for the interaction of two quasimonomers k and l which differs from B^*, the corresponding difference being proportional to $\nu(\Delta n_k \nu) + \nu(\Delta n_e \nu)$, where Δn_i is the excess of local monomer density near the ith bare monomer over the local density which would occur at this point in the case of an infinite linear chain.

Thus the problem splits into the following two parts. First of all it is necessary to obtain the values of Δn_i for each monomer of the macromolecule. Then we must calculate the conformational characteristics of the macromolecule (to be precise we shall deal further with the expansion factor, α, with respect to the completely unperturbed dimensions), taking into account the fact that the monomers k and l of this macromolecule interact with a second virial coefficient:

$$B^* + \text{constant}\ [(\Delta n_k \nu)\nu + (\Delta n_e \nu)\nu] \qquad (3)$$

(constant = a numerical constant of order unity). Each of these two parts of the problem is solved by standard methods, here we shall describe them only briefly.

It is easy to obtain local monomer densities in the completely unperturbed state, when all the chains of a branched macromolecule are gaussian coils. However, it turns out that even near the θ point of a linear polymer the branched macromolecule is not really unperturbed, but expands due to the additional repulsion described above. Thus the question arises: how do we obtain the local density for the expanded macromolecule? It is natural to assume in this case that the local density is equal to the unperturbed local density divided by $(\alpha')^1$ is the expansion factor of the part of macromolecule; the monomers of this section are responsible for the main contribution to the excess density Δn (α' is not necessarily equal to α, the expansion factor of the entire macromolecule). In particular, for the comb-branched macromolecule with $\sigma \gg 1$ (i.e. for the thick comb) the main contribution to Δn for the majority of monomers is due to those monomers which are situated in the section of the comb surrounding a given monomer of the type encircled by a dotted line in *Figure 5* (the length of this section along the backbone is of the same order as the length of branches). We call the spatial organization of the comb-like molecule on this level its secondary structure[17]. We can see that the value of α' mentioned above is in this case the expansion factor on the level of secondary structure. Using this procedure α' appears in equation (5) for the expansion factor, α, of the entire comb-like macromolecule, in the case $\sigma \gg 1$ (for the calculation of α^1 see below).

The second part of the problem is the determination of the expansion factor of the macromolecule, the second virial

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* It must be noted that the effective attraction due to the finite nature of branches and of the backbone also exists here, but the simple analysis shows that it is always much weaker than the effective repulsion; thus we shall not take it into account further

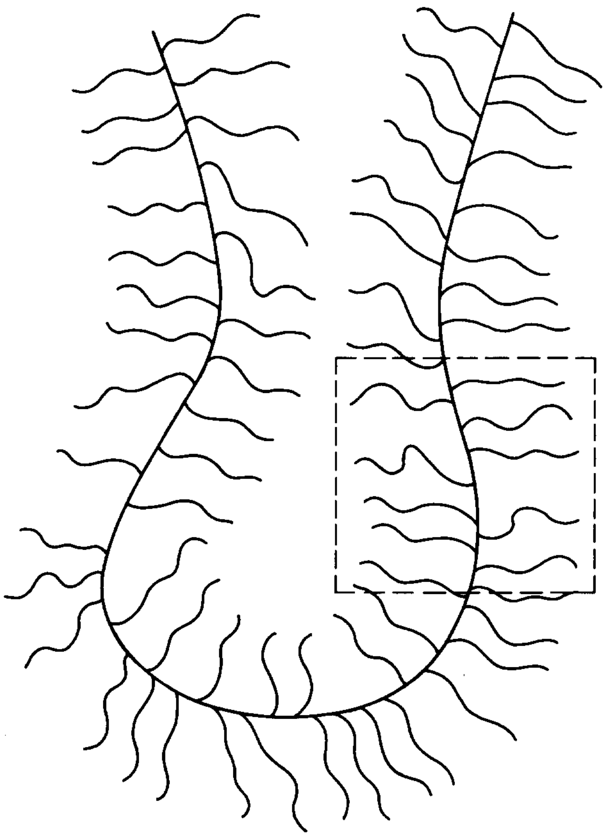

Figure 5 Comb-like macromolecule. The section of 'secondary structure' is encircled by the dotted line

coefficient (equation 3) of the interaction of each pair of monomers being known. This can be carried out by means of the standard Flory method[1] modified by Ptitsyn[16]. This method is well known, so we shall not reproduce the corresponding calculation here, but simply quote the equation obtained for α. This equation has different forms depending on the value of σ, due to the different geometries of the macromolecules:

(a) Case 1: $\sigma \ll 1$ (the thin comb)

$$\alpha^5 - \alpha^3 = \tau N^{1/2} + (n\sigma)^{1/2} \tag{4}$$

(b) Case 2: $1 \ll \sigma \ll n$ (the thick comb)

$$\alpha^5 - \alpha^3 = \tau N^{1/2}\sigma^{3/2} + n^{1/2}\sigma^{5/2}(\alpha')^{-3} \tag{5}$$

(c) Case 3: $\sigma \gg n$ (the star)

$$\alpha^5 - \alpha^3 = \tau N^{1/2} n^{3/2} + n^3\alpha^{-3} \tag{6}$$

Here $\tau = (T - \theta)/T$, where θ is the true θ temperature for the linear polymer (i.e. $B^* = 0$ at $T = \theta$).

It must be noted that all the numerical coefficients of the terms on the right-hand sides of equations (4)–(6) have been omitted. In fact for flexible chains there is a numerical factor of the order of unity before each term (i.e. for the case $v \sim a^3$), which is constant for a given polymer–solvent system. The first term on the right-hand side of equations (4)–(6) is the same as in the Flory–Ptitsyn theory[16]. This would be the only term if the second virial coefficient of the interaction of all the quasimonomers were equal to B^*. The second term is the specific correction, which appears due to the corrections to B^* in equation (3).

In equation (5) we still have the unknown coefficient α' – the expansion factor due to the monomer–monomer interaction for the secondary structure. The number of monomers in the region of secondary structure, encircled with a dotted line in *Figure 5*, is of order $\sim \sigma N/n$ and the number of branches $n' \sim \sigma$; thus the same equation as for the star with σ branches and the total number of monomers $\sim \sigma N/n$ must be valid for α' in the orders of magnitude, i.e.:

$$(\alpha')^5 - (\alpha')^3 = \tau\left(N\frac{\sigma}{n}\right)^{1/2}\sigma^{3/2} + \sigma^3(\alpha')^{-3} \tag{7}$$

The solution α' of this equation is substituted into equation (5).

We now discuss the difference between the corrections to the Flory–Ptitsyn equations obtained in this work and in ref 15 where the anomalous θ behaviour of branched polymers was attributed to the influence of three body interactions of the remote parts of the chain. The order of magnitude of the corresponding corrections can be obtained if in all the Flory–Ptitsyn expressions B^* is replaced by $B^* + (nv)v$, where n is the average monomer density in the coil. At the same time, in our approach, B^* is replaced by a term of order $B^* + (\Delta nv)v$, where Δn is the local monomer density near the given monomer minus the local density in the case of an infinite linear chain. It is easy to see that for comb-branched polymers $\Delta n \gg n$ and thus our correction is much more essential than that obtained in ref 15; however for star-branched polymers $\Delta n \sim n$, and thus both approaches must give corrections of the same order of magnitude.

Hence it is clear that the theory[15] is in satisfactory agreement with experiment in the case of star-branched polymers and fails to predict the correct results for comb-branched polymers. For star-branched polymers the corrections obtained in ref 15 had the correct order of magnitude and the correct dependence on n and α. For comb-branched polymers these corrections are much smaller than the corrections in equations (4) and (5).

From equations (4)–(7) it is easy to obtain the necessary information concerning the expansion of branched polymers. First let us consider the value, α_θ, of the expansion at the true θ point of a linear polymer ($\tau = 0$). From these equations it follows for each of three cases:

$$\begin{aligned} &\text{Case 1:}\quad \alpha_\theta^5 - \alpha_\theta^3 \sim (n\sigma)^{1/2} \\ &\text{Case 2:}\quad \alpha_\theta^5 - \alpha_\theta^3 \sim n^{1/2}\sigma^{11/8} \\ &\text{Case 3:}\quad \alpha_\theta^8 - \alpha_\theta^6 \sim n^3 \end{aligned} \tag{8}$$

The value of the relative lowering of the θ_α temperature $\tau_\alpha = (\theta - \theta_\alpha)/\theta$, determined by the condition $\alpha^2 = 1$, appears to be equal for each of three cases:

$$\begin{aligned} &\text{Case 1:}\quad \tau_\alpha \sim (n\sigma)^{1/2} N^{-1/2} \\ &\text{Case 2:}\quad \tau_\alpha \sim (n/N)^{1/2}\cdot\sigma \\ &\text{Case 3:}\quad \tau_\alpha \sim n^{3/2} N^{-1/2} \end{aligned} \tag{9}$$

The relative lowering τ_{A_2} of the θ_{A_2} temperature, determined by the condition $A_2 = 0$, turns out to be of the same order ($\tau_{A_2} \sim \tau_\alpha$) but with a different numerical coefficient. (τ_{A_2} can be obtained from the generalization of the Flory theory of the excluded volume of a polymeric coil[1], analo-

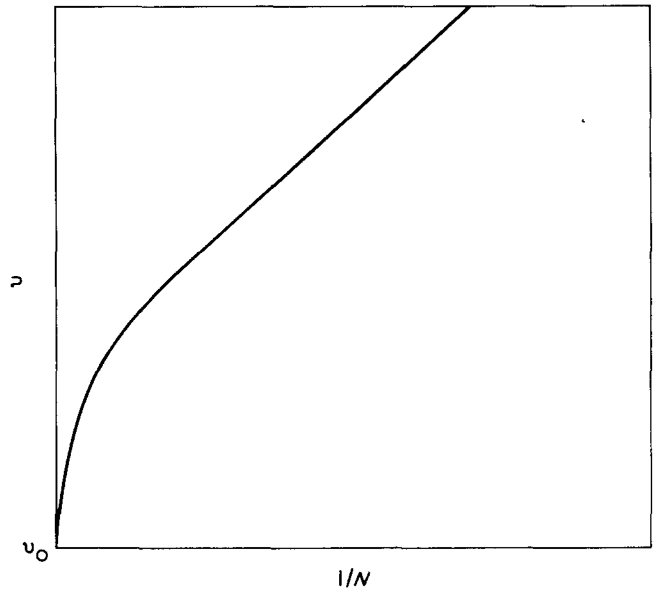

Figure 6 Dependence of $\tilde{\nu}$ on N^{-1} obtained in ref 18

gous to the above generalization of the Flory calculation for α^2.) The same conclusion can also be drawn for the lowering of the θ temperature determined by any other condition. Thus equations (9) determine the width of the θ region for branched polymers. In contrast to the linear case the true θ temperature is here situated at the upper boundary of this θ region.

As to the comparison of equations (8) and (9) with the experimental data in ref 15 (for θ_α, θ_{A_2}, and α_θ), the theory developed allows to diminish considerably the deviations from experiment in comparison with the theory[15]. However, we do not set out here the corresponding calculations, because in order to test equations (8) and (9) it is necessary to perform numerous measurements in each of three regions of variating σ.

The theory developed above deals only with the θ behaviour of branched polymers. It turns out that this theory cannot be directly applied to the good solvent behaviour of branched polymers, which is considered in Appendix 2.

PARTIAL SPECIFIC VOLUME

In this section we shall consider the dependence of partial specific volume $\tilde{\nu}$ of polymer solutions (i.e. the volume per monomer) on the number of monomers N, in the macromolecule. It turns out that this problem can be analysed by methods analogous to those described above.

For linear macromolecules we expect the following dependence of partial specific volume on N:

$$\tilde{\nu} = \nu_0 + K/N \tag{10}$$

where the second term is due to the presence of anomalous groups at the ends of the chain. (K is used in this section to denote the constants, which are independent of N.) However, in experiments 18–20 it was noticed that the dependence $\tilde{\nu}(N)$ (as well as $dn/dc(N)$, where dn/dc is the refractive index increment – its value is connected with $\tilde{\nu}$) has the form shown in *Figure 6*, which indicates that there are terms in $\tilde{\nu}$ decreasing at large N more slowly than N^{-1}.

In order to explain this fact it was assumed in ref 18, that each monomer–monomer contact in the coil is accompanied by the formation of 'free volume' which is inaccessible for the molecules of solvent. If this is the case we can write an expression for the partial specific volume:

$$\tilde{\nu} = \nu_0 + \frac{K}{N} + K'S \tag{11}$$

where S is the average probability of the contact per monomer.

However, in ref 18 is was assumed that S is proportional to the average monomer density in the coil, whereas it is clear that S is proportional to the local monomer density. Thus, in order to test the validity of this hypothesis of the free volume, it is necessary to reconsider the expression for S proposed in ref 18.

The value of S can be obtained with the help of arguments analogous to those used above, when the concept of quasimonomers was introduced. For infinite chains the average probability of the contact per monomer is some finite value, S^*, the main contribution to S^* being from contacts between monomers which are close to each other along the chain. We then consider a finite chain of N monomers. For this chain, the probability S for each monomer of the chain is less than S^*, because there is no contribution to S from contacts with the parts of the chain which would be present in the case of an infinite chain (compare with *Figure 4*). By analogy to our treatment in the previous sections it is easy to see that $(S^* - S_i)/S^* \sim i^{-1/2}\alpha^{-3}$, where i is the number of monomers between the given monomer and the nearest chain-end, S_i is the probability of contact for a given monomer and α is the expansion factor of the coil. Thus the average contact probability, S, is equal to:

$$S = S^* - \frac{K''}{N^{1/2}\alpha^3} \tag{12}$$

Substituting equation (12) into (11), we obtain for the partial specific volume:

$$\tilde{\nu} = (\nu_0 + K'S^*) + \frac{K}{N} - \frac{K''K'}{N^{1/2}\alpha^3} \tag{13}$$

The last term decreases more slowly than N^{-1} when $N \to \infty$.

It must be noted that according to equation (12) the average probability of contact increases with N. At the same time, experiment 18 shows that $\tilde{\nu}$ decreases with N. Thus, in order to relate equation (13) to the experimentally observed behaviour it is necessary to assume that $K' < 0$, i.e. that the free volume is negative. This means that two monomers in contact occupy a smaller effective volume than two separated monomers.

Further analysis of experimental data obtained in ref 18 however, shows that the hypothesis of a negative free volume is also unsatisfactory. If this hypothesis were valid, then the increase in the degree of branching would lead to a decrease of $\tilde{\nu}$; however, experiment shows the reverse trend[18,20]. Moreover, the value of $\tilde{\nu}$ should be strongly dependent on the polymer concentration in the solution – this also was not observed experimentally[18].

Thus the comparison of the results obtained by correct calculation of the number of contacts in a polymeric coil with experimental data shows that the effects, which were observed in refs 18–20, are not connected with the formation of positive or negative free volume between the monomers in contact.

In the author's opinion the anomalous variation of the partial specific volume with N is due to the dependence of the relative number of rotational isomers on the expansion factor of the coil α. This will be developed in detail in a separate publication.

CONCLUSIONS

The concept of quasimonomers has been introduced, i.e. the concept of disconnected quasiparticles, which can be effectively substituted for a chain of connected monomers,. Such a substitution becomes possible because each monomer of an infinite homogeneous chain is 'standardly surrounded' by the other monomers (primarily by the close neighbours along the chain) and by the solvent molecules. This 'standard surrounding' renormalizes the monomer characteristics in such a way that each monomer can be regarded as a disconnected quasiparticle in the analysis of some effects of monomer–monomer interaction in the coil. The properties of this quasiparticle are not the same as the properties of the initial monomer. The advantage of quasimonomers over monomers is that their concentration in any volume is small due to their disconnectivity; thus the interaction in the cloud of quasimonomers can be characterized by means of a virial expansion.

The concept of quasimonomers turns out to be useful in the analysis of inhomogeneous polymer chains (finite chains, chains with defects, branched chains). If the chain is not infinite and homogeneous, then the 'standard surrounding' of all the monomers changes. However, for the majority of monomers this change is small, so that the characteristics of the corresponding quasimonomers (for example, their virial coefficients B^*, C^* . . .) can be assumed to vary linearly with the variation of local density Δn near the given monomer. After the variation of Δn and, consequently, of B^*, C^* . . . is found, it is easy to calculate the effect of monomer–monomer interactions on any conformational characteristic by means of classical methods, i.e. using the picture of the polymeric coil as a cloud of disconnected particles with known interactions effectively changed due to the inhomogeneity of the chain.

It must be noted that the value of Δn depends on the distance between the given monomer and the closest inhomogeneity. Thus the characteristics of the interaction of quasimonomer depends on the position of the corresponding bare monomer in the chain.

Only some of the problems for which the concept of quasimonomers can be useful were considered in this paper. We expect that the same methods can be applied to the analysis of other problems, in which the departure of the polymer chain from the infinite homogeneous structure is present. The theory of block copolymer solutions and the theory of polymer solutions in mixed solvents can be regarded as examples of this kind. As to the concentrated polymer solutions, here it is interesting to relate the concept of quasimonomers and the new Flory theory.

Finally, the method of quasimonomers has been used together with the classical methods (perturbation theory, Flory theory). It would be very interesting to include the concept of quasimonomers in the general picture of the polymer–magnetic analogy[21–22,4] and to calculate the conformational properties by means of the consistent renormalization group approach, because it is well-known that such a calculation gives more exact results than the classical methods. This will be the subject of a further study.

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REFERENCES

1 Flory, P. J. 'Principles of polymer chemistry', Cornell University Press, Ithaca, New York, 1953
2 Flory, P. J. *Discuss. Faraday Soc.* 1970, **49**, 7
3 Khokhlov, A. R. *J. Phys. (Paris)* 1977, **38**, 845
4 Lifshitz, I. M., Grosberg, A. Yu. and Khokhlov, A. R. *Rev. Mod. Phys.* 1978, **50**, No. 3, Chapter II
5 Gotlib, Yu. Ya. and Skvortsov, A. M., *Vysokomolek. Soedin (A)* 1976,**18**, 1971
6 Yamakawa, H., 'Modern theory of polymer solutions', Wiley, New York, 1971
7 Oyama, T. and Oono, Y. *J. Phys. Soc. Jpn* 1977, **42**, 1348
8 McCrackin, F. L., Mazur, J. and Guttman, C. M. *Macromolecules* 1973, **6**, 859
9 Clark, A. T. and Lal, M., *Br. Polym. J.* 1977, **9**, 92
10 Janssens, M. and Bellemans, A. *Macromolecules* 1976, **9**, 303
11 Olaj, O. F. and Pelinka, K. H. *Makromol. Chem.* 1976, **177**, 3413
12 Olaj, O. F. *Makromol. Chem.* 1976, **177**, 3427
13 Rapaport, D. C. *Macromolecules* 1974, **7**, 64
14 Roovers, J. E. L. and Bywater, S. *Macromolecules* 1976, **9**, 873
15 Candau, F., Rempp, P. and Benoit, H. *Macromolecules* 1972, **5**, 627
16 Ptitsyn, O. B. *Zh. Fiz. Chim.* 1955, **29**, 396
17 Khokhlov, A. R. *Vysokomolek, Soedin (A)* 1978, **20**, 1860
18 Francois, J., Candau, F. and Benoit, H. *Polymer* 1974, **15**, 618
19 Candau, F., Francois, J. and Benoit, H. *Polymer* 1974, **15**, 626
20 Candau, F., Dufour, C. and Francois, J. *Makromol. Chem.* 1976, **177**,3359
21 McKenzie, D. S. *Phys. Reports* 1976, **27**, 35
22 de Gennes, P. G. *Riv. Nuovo Cimento* 1977, **7**, 363
23 Khokhlov, A. R. *Vysokomol. Soedin (A)* 1978, **20**, No. 12
24 Leemput, R. V. and Meunier, J. *Makromol. Chem.* 1971. **147**, 191
25 Mazur, J. and McCrackin, F. *Macromolecules* 1977, **10**, 326
26 Daoud, M. and Jannink, G. *J. Phys. (Paris)* 1976, **37**, 973

APPENDIX 1

Relation between different polymer chain models

We consider here whether it is possible to find an equivalent chain of beads for each polymer chain in such a way that all the macroscopic confomational characteristics of the two corresponding coils coincide.

It is well-known that in the model of beads with correlations given by equation (1), the macroscopic conformational characteristics of a polymeric coil depend (in the universality region $T > \theta$) only on two combinations of the parameters of the model: Na^2 and $N^{1/2}B^*/a^3$. It was shown above, that a dependence only on the effective coefficient B^* among all the characteristics of monomer–monomer volume interaction is a general property of all polymeric coils. Thus we assume that the dependence of macroscopic characteristics on only two combinations of the parameters (analogous to Na^2 and $N^{1/2}B^*/a^3$ in the model of beads) is also a general property of every coil. This is the basic assumption of the so-called two parameter theory.

It must be noted that the two combinations of parameters have a definite physical meaning for the model of beads: Na^2 is equal to $\langle R^2\rangle_0$, i.e. to the mean square end-to-end distance in the absence of volume interactions, and $Z = N^{1/2}B^*/a^3$ is a single-valued function of the expansion factor of the coil, (see ref 4)

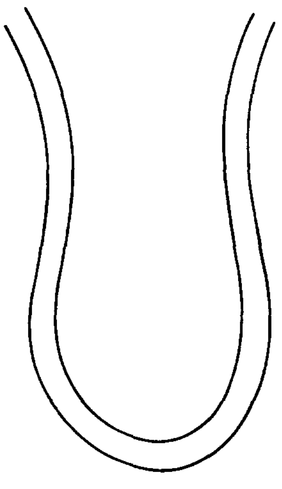

Figure A1 Persistence model of a polymer chain

$$\alpha^2 = \alpha^2(Z) \equiv \langle R^2\rangle / \langle R^2\rangle_0$$

Thus if the assumption of the two-parameter theory is valid, it is possible to find a chain of beads which is equivalent to the given chain: one must choose the parameters describing the chain of beads in such a way that the values of $\langle R^2\rangle_0$ and α^2 will be the same as for the initial chain. Then all the other macroscopic conformational characteristics of the coil of beads and of the initial coil will also coincide, i.e. these two chains will be equivalent.

Since in order to specify the chain of beads it is necessary to assign three parameters N, a and B^*, and we have imposed only two conditions, one of these parameters can be chosen arbitrarily. This corresponds to the fact that the initial chain can be arbitrarily divided into monomers, i.e. the value of N can be chosen arbitrarily, but the values of a and B^* are definite for a given N. The choice of an elementary monomer must satisfy only one condition, viz. it is necessary that this monomer does not interact with itself, otherwise it certainly will not be an elementary monomer. For example, one cannot choose an elementary monomer of length greater than the persistence length of the chain.

As an example, we consider the persistence model of a polymer chain and find the equivalent model of beads for it. In the persistence model the polymer chain is represented as a long flexible elastic filament of width d and of persistence length l (*Figure A1*). The sections of this chain interact with some linear density of interaction. It is clear that such a model is more realistic than the model of beads.

First of all, it is necessary to determine the method of dividing of the persistence chain into monomers. Since for this chain we have two characteristic lengths d and l, we divide the chain either into sections of length l or into sections of length, d. In these two cases we shall obtain two different but equivalent chains of beads.

First let the chain be divided into sections of length l (Case 1). Then N_1 is the number of persistence lengths in the chain $N_1 = L/l$, where L is the total length of the chain. Since in this case $\langle R^2\rangle_0 = N_1 l^2$, in order to satisfy the condition of coincidence between $\langle R^2\rangle_0$ for the persistence chain and for the equivalent chain of beads, we have to choose $a_1 = l$. The parameter B^* will in this case coincide in order of magnitude with the second virial coefficient of the interaction of cylinders of diameter d and of length l, i.e. $B_1^* \sim dl^2\tau$, where $\tau = (T - \theta)/\theta$. Thus all the parameters for the equivalent model of beads are determined. Analysis of the properties of the persistence model with the help of the equivalent chain of beads just determined can be found in ref 23.

We now divide the persistence chain into pieces of length d (Case 2); hence $N_2 = L/d$. Since in this case

$$\langle R^2\rangle_0 = \frac{N_2}{l} dl^2 = Npd^2$$

where $p = l/d$, we must choose $a_2 = p^{1/2}d$. B_2^* for this case can be found from the condition $Z_1 = Z_2$, i.e.:

$$N_1^{1/2}B_1^*/a_1^3 = N_2^{1/2}B_2^*/a_2^3$$

It follows from this equation that $B_2^* \sim d^3\tau$.

In physical applications, either the first or the second representation of the polymer chain can be used.

It should be pointed out that for flexible chains $l \sim d$, so there is no difference between these two representations. If we take into account the estimation $B^* \sim v\tau$, it turns out that in the case of the equivalent chain of beads we have $v \sim a^3$, i.e. this chain is of the type shown in *Figure 3a*. The size of each bead is $\sim d$ and the number of beads is equal to the length to width ratio of the chain.

For stiff chains $p = l/d \gg 1$ and thus in both representations $v \ll a^3$, so the equivalent chain of beads is of the type shown in *Figure 3b*. The properties of the coil of beads and of the persistence stiff chain coil are, of course, equivalent only in the absence of orientational ordering, i.e. in the absence of the intramolecular liquid–crystalline phase.

APPENDIX 2

Expansion factor for branched macromolecules in good solvents

Equations (4)–(6) seem to be valid for good solvents; in this case the second term on the right-hand side is much smaller than the first and can be neglected. Thus we arrive at the usual Flory–Ptitsyn equations[16]:

$$\text{Case 1:}\quad \alpha^5 - \alpha^3 \sim \tau N^{1/2}$$

$$\text{Case 2:}\quad \alpha^5 - \alpha^3 \sim \tau N^{1/2}\sigma^{3/2}$$

$$\text{Case 3:}\quad \alpha^5 - \alpha^3 \sim \tau N^{1/2}\sigma^{3/2} \tag{A1}$$

It can be seen from (A1) that according to the Flory–Ptitsyn theory the expansion factor of a branched macromolecule, α, is greater than that of a linear macromolecule of the same molecular weight and increases with an increase in the degree of branching.

At the same time experimental data[24] show the opposite trend. Recently, a direct computer experiment for star-branched polymers was carried out and it was revealed that these macromolecules expand less in a good solvent than linear macromolecules of the same molecular weight, the expansion factor decreasing with an increase in the degree of branching. Below we shall try to explain this fact and to develop a simple theory of the expansion of branched macromolecules in good solvents.

The average monomer concentration within the branched macromolecule is essentially higher than within the linear one. Thus it turns out that each of the linear chains which form the branched macromolecule, is situated in a concentrated solution of other chains, the concentration corresponding (from the local point of view) to the semidilute polymer solution. It is well-known that in the semidilute region the expansion factor of a linear macromolecule decreases with an increase in the average monomer concentration in the solution, c[26]:

$$(\alpha')^2 \sim (cv)^{-1/4}\tau^{1/4} \tag{A2}$$

where v is the volume of a monomer. We suppose that it is this concentration-dependent decrease in the dimensions of linear chains forming the branched macromolecules which is responsible for the smaller expansion of branched polymers in good solvents in comparison with linear polymers.

We shall consider in detail the relatively more complex Case 2 ($1 \ll \sigma \ll n$); for other cases we shall give only the final result.

The expansion factor of the macromolecule in Case 2 (a thick comb) is calculated in two steps. In the first step we obtain the expansion factor α' of the section of secondary structure encircled with a dotted line in *Figure 5* due to the repulsion of monomers within this section. Thus we determine the parameters of the worm-like filament (its width and its persistence length, which are of the same order in this case), which can be substituted for the comb-like macromolecule. We consider this filament to be impenetrable in the good solvent region. In the second step the expansion factor α'' of the worm-like impenetrable filament is determined using the standard methods. The expansion factor of the entire macromolecule (which approximately coincides with the expansion factor of the backbone) is equal to the product of α' and α'': $\alpha = \alpha'\alpha''$.

We therefore consider the section of secondary structure which has a length along the backbone of the same order as the length of branches (*Figure 5*). In this section there are $\sim\sigma$ linear side chains, each of these chains containing $\sim N/n$ monomers. The average concentration c of monomers in this section is equal to:

$$c \sim \frac{\frac{N}{n}\sigma}{(\alpha')^3 L_0^3} \sim \frac{1}{(\alpha')^3 a^3}\left(\frac{n}{N}\right)^{1/2}\sigma \tag{A3}$$

where $L_0 \sim (N/n)^{1/2}a$ gives the unperturbed dimensions of this section. On the other hand, the concentration in equation (A3) corresponds to the region of semidilute solutions (this can be verified after the final result is obtained), thus equation (A2) must be valid for α'. Eliminating c from equations (A2) and (A3), we have:

$$(\alpha')^5 \sim \left(\frac{N}{n}\right)^{1/2}\frac{\tau}{\sigma} \tag{A4}$$

The expansion factor α'' in the second step can be determined by usual methods. Asymptotically, at high α'':

$$(\alpha'')^5 \sim \tilde{N}^{1/2} \sim (n/\sigma)^{1/2}$$

where $\tilde{N} = n/\sigma$ is the number of persistence lengths in the worm-like filament. Thus:

$$\alpha^5 = (\alpha')^5(\alpha'')^5 = \tau N^{1/2}\sigma^{-3/2} \tag{A5}$$

The result (equation A5) is asymptotically valid at $\alpha \gg 1$. It can be written in the more usual Flory form:

$$\alpha^5 - \alpha^3 = \text{constant} \times \frac{\tau N^{1/2}}{\sigma^{-3/2}} \tag{A6}$$

It is necessary, however, to bear in mind that equation (A6) is not valid at small τ, because equation (A2) can be applied only to the region of semidilute solutions in good solvents (the temperature–concentration boundaries of this region have been specified in ref 26).

For the star-like polymer ($\sigma \gg n$) we obtain the analogous result:

$$\alpha^5 - \alpha^3 = \text{constant} \times \frac{\tau N^{1/2}}{n^{3/2}} \tag{A7}$$

For comb-like polymers with $\sigma \ll 1$ it turns out that α does not change considerably in comparison with the case of linear polymers:

$$\alpha^5 - \alpha^3 = \text{constant} \times \tau N^{1/2} \tag{A8}$$

It is seen from equations (A6)–(A8) that the value of α for the branched polymer is smaller than for the linear polymer with the same N and decreases with an increase in the degree of branching. This is in agreement with the experimentally observed behaviour.

Equations (A6)–(A8), which take into account the concentration-dependent decrease of the dimensions of chains forming the branched macromolecule, differ considerably from equations (A1) of the Flory–Ptitsyn theory, which is thus not valid in the good solvent region. This is a consequence of the fact that the behaviour of semidilute good solutions cannot be correctly described by means of mean field theories (in particular, by means of the Flory theory) – equation (A2) is not valid in these theories[26]. At the same time the mean field theories are qualitatively valid in the vicinity of the θ point[26]. Thus the Flory-type theory can be used in the analysis of the θ behaviour of branched macromolecules (see above).