Translated from *Uspekhi Khimii*, **46**, 1279-1301 (1977) U.D.C. 541.6 : 547.913

Fundamental Hydrodynamic Characteristics of Polymers with Star and Comb Macromolecular Structures

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The review considers the majority of studies published up to 1976 and dealing with the hydrodynamic properties of polymers having star and comb macromolecular structures. Methods for the estimation of the degree of branching are presented and it is shown how the dependence of the intrinsic viscosity on molecular weight changes on passing from randomly branched macromolecules to star and comb macromolecules. The influence of the polydispersity of the branches on the size of the macromolecules and their rigidity parameters is examined.
The bibliography includes 110 references.

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NOTATION

η_0 = solvent viscosity;
$[\eta]$ = intrinsic viscosity of the polymer solution;
$[\eta]_\theta, [\eta]_l, [\eta]_g$ = intrinsic viscosities in a θ-solvent and of linear and branched macromolecules respectively;
M = molecular weight (M.W.); $\overline{M}_n$, $\overline{M}_w$, and $\overline{M}_z$ are the number-average, weight-average, and z-average molecular weights;
A = Kuhn segment; A_l, A_g, A_s, and A_b are the corresponding segments for linear and branched macromolecules and in the main and side chains of a branched macromolecule ("backbone" and "branches");
S = number of monomeric units in the Kuhn segment; S_s is the corresponding number for the main chain of a branched macromolecule;
a = persistent length (correlation length);
L = contour length of the macromolecule (the length of the macromolecule straightened without distortion of the valence angles); L_s and L_b are the corresponding values for the main and side chains;
l = distance between two neighbouring branches;
λ = projection of the monomeric unit in the direction of the main chain;
$[\overline{R}^2]^{1/2}$ = mean square radius of inertia; $[\overline{R}^2]_l^{1/2}$ and $[\overline{R}^2]_g^{1/2}$ are the corresponding radii for the linear and branched macromolecule;
$[\overline{h}^2]^{1/2}$ = mean square distance between the ends of the macromolecules;
g = factor characterising the degree of branching of the macromolecule;
ϵ = swelling parameter of the polymeric coil;
N = number of Kuhn segments in the macromolecule; N_s and N_b are the corresponding numbers for the main and side chains;
f = number of branches in the branched macromolecule;
m = average number of branching centres (points) per macromolecule;
Φ = Flory constant;
h = ratio of the hydrodynamic radii of the branched and linear macromolecules with the same degrees of polymerisation;
P = degree of polymerisation;
F = translational friction constant;
α = swelling coefficient;
χ = parameter characterising the excess energy of the interaction of macromolecules in solution per solvent molecule;
z = parameter characterising the number of collisions of the chain units within the limits of the coil per unit volume;
γ = effective excluded volume of the segment;
μ = chemical potential of the system;
C_m = coefficient of polymer–solvent interaction:

$$C_m = \left(\frac{3^3}{2^{5/2}\pi^{3/2}}\right)\left(\frac{\bar{v}^2}{V_1 \cdot N_A}\right)\left(\frac{M}{\overline{h}_\theta^2}\right)^{3/2},$$

Here the symbols have the following significance:
V_1 = molar volume of the solvent; N_A = Avogadro number;
v = specific partial volume of the polymer;
ψ_1 = entropy parameter of the system;
T = temperature of the solution;
A_2 = second virial coefficient in the expansion of the osmotic pressure in terms of concentration;
a, b, K_η, K_s = parameters of the equation relating $[\eta]$ to M;
φ = variable.

I. INTRODUCTION

The extensive development of the theory and practical applications of anionic polymerisation made it possible to obtain polymers with a strictly specified macromolecular structure. Thus virtually monodisperse polystyrenes have now been synthesised and investigated in detail[1-5]. The anionic polymerisation of organocyclosiloxanes in the presence of tri- and tetra-functional sodium initiators led to the synthesis of star polydimethylsiloxanes with a narrow molecular weight distribution (MWD).[6-9] The use of a trifunctional activator for the synthesis of branched polyamides[10] and the synthesis of a star dextran[11] and a star polyethylene[12] have been described.

The synthesis of polymers with a comb macromolecular structure has been developed on an even larger scale during the last decade. Numerous studies were published between 1965 and 1975, in which the properties of comb polymers and the difference of their behaviour in solution from that of polymers with a linear macromolecular structure were discussed.

The behaviour of polymers in solution is determined by many factors, the main ones being the chemical structure and the geometry of the macromolecules, the nature of the solvent, the molecular weight (M.W.) of the polymer, and the temperature of the solution. Thus the introduction of only a few long branches into the macromolecule of a linear polymer leads to an appreciable decrease in the size of the molecular coil in solution and hence to a decrease of $[\eta]$ relative to the linear polymer with the same chemical composition[13]. The most reliable data on the degree of branching of macromolecules can therefore be obtained by studying the properties of dilute solutions of polymers and the dependence of these properties on the size and number of branches in the macromolecule[4,13-20].

However, a quantitative interpretation of the experimental results is in most cases extremely difficult. A common disadvantage of the existing methods is the necessity to compare the results with the corresponding results for linear polymers having the same chemical composition and molecular weight[13].

If a branched macromolecule does not obey Gaussian statistics, it is necessary to compare the dimensions of molecules having not only the same molecular weight but also the same thermodynamic rigidity, i.e. with $A_g = A_l$. One must then take into account also the thermodynamic rigidity of the main (A_s) and side (A_b) chains of the branched macromolecule[21].

In certain cases, it is convenient to compare the experimental characteristics of the branched macromolecules with the analogous characteristics of the linear molecules whose molecular weight is equal to that of the main chain of the branched macromolecule, i.e. of the "backbone".[21]

The problem of determining the influence of the degree of branching on the parameters of the macromolecular coil is complicated by the existence of a wide variety of types of branching. It is usual to distinguish three types of branching: star, comb, and cascade branching[22-26]. In the comb and cascade branching, the molecule contains not one but several branching nodes, in contrast to star branching. Regular (equal lengths of the branches) and random (different lengths of the branches) structures are also characteristic of these three types of branching. One of the types of regular star branching has been examined by Tsvetkov[27]. In addition, it is possible to distinguish long-chain and short-chain branching. In certain cases, short-chain branching has only an insignificant influence on the properties of macromolecules in solution[24-26].

All the comb polymers known at present can be divided into two types: comb homopolymers and graft comb heteropolymers (copolymers). Comb homopolymers include polymers whose macromolecules have long straight-chain aliphatic side branches in each monomeric unit, for example, poly-α-olefins, poly(alkyl acrylates), polyvinyl ethers, polyvinyl esters, etc.[28-39]. The structures of graft comb copolymers depend on the molecular parameters of the homopolymers incorporated in them[40-48].

Fairly numerous experimental studies of the properties in solution of polymers with the comb macromolecular structure have now been published[18,19,25,28-51]. However, the hydrodynamics of solutions of star polymers have been investigated only in relation to polystyrene[1-5,52] and polyorganosiloxanes[6-9].

Macromolecules with cascade random branching are the type most frequently synthesised. At high degrees of conversion, such macromolecules can be transformed into microgels and gels.

A comparative examination of the hydrodynamics of solutions of polymers with the comb and star macromolecular structures on the basis of the available theoretical[3,22,23,25,50-52,54,55] and experimental[2,18,19,21,25,53,56-60] data is of undoubted interest. For all types of branching, the dimensions of macromolecules are characterised solely by their average radius of inertia $[\bar{R}^2]_g^{1/2}$, since the concept of the distance between the ends of the polymer chain $[\bar{h}^2]^{1/2}$, defining the size of linear macromolecules, loses its significance in the present instance[22,24,57]. Usually $[\bar{R}^2]_g^{1/2} < [\bar{R}^2]_l^{1/2}$, so that the intrinsic viscosity $[\eta]_g < [\eta]_l$.

The degree of branching of macromolecules has come to be characterised by the factor g[22,25,50,55]:

$$g^{\epsilon} \simeq [\bar{R}_0^2]_g/[\bar{R}_0^2]_l \text{ and } g^{\circ} = [\eta_\theta]_g/[\eta_\theta]_l, \qquad (1)$$

where ϵ may assume values of 1/2, 1, and 3/2. The factor g is determined by the number of segments in the backbone of the macromolecule and in the branches[61,62]:

$$g = \frac{N - \sum_b N_b}{N} = \frac{N_s}{N}.$$

However, the factor g depends also on the number, rigidity, and polydispersity of the side branches, and on the length, rigidity, and polydispersity of the main chain[61].

Depending on the type of branching, short side branches, which usually do not have a significant influence on the macromolecular size, can affect the values of $[\bar{R}_\theta]_g^2$ in a θ-solvent[50,51-54,56-60]. On the other hand, in effective solvents the presence of short branches can appreciably increase the size of the macromolecule[56-58].

II. STAR MACROMOLECULES

Three-, tetra-, and poly-functional star macromolecules with single and multiple branching centres are known. Star macromolecules may be homogeneous, with the centre of the star and the branches consisting of atoms of the same kind (Fig. 1*a*), and heterogeneous (Fig. 1*b*). The branches of the star may be of the same or different length, short and long, mono- and poly-disperse.

In 1949, Zimm and Stockmayer[50] suggested that the degree of branching of homogeneous star polymers whose molecules have different branching functionalities (tri- and tetra-functional branching) be characterised by a quantity

g proportional to the ratio of the mean square radii of inertia of the branched and linear macromolecules and to the ratio of the intrinsic viscosities:

$$g^{3/2} \simeq ([\overline{R}^2_\theta]_g/[\overline{R}^2_\theta]_l)^{3/2}; \; g^{3/2} = [\eta_\theta]_g/[\eta_\theta]_l. \qquad (2)$$

The use of this relation is based on the hypothesis that the Flory equation for linear polymers [63]

$$[\eta_\theta]_l = \Phi_\theta [\overline{R}^2_\theta]^{3/2}_l/M$$

is valid also for branched specimens.

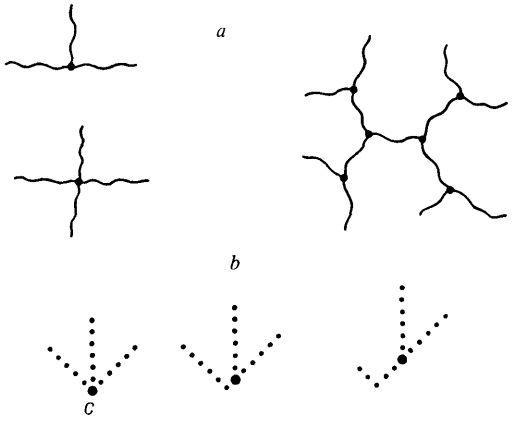


Figure 1. Graphical representation of the possible structures of a star macromolecule: *a*) homogeneous branching [27]; *b*) heterogeneous branching [98]; *c*) centre of the star.

However, Stockmayer and Fixmann [54] and Zimm and Kilb [27,55] showed that the effective hydrodynamic radius of the polymeric molecule is less sensitive to branching than the radius of inertia $[\overline{R}^2_\theta]^{1/2}$. In this case, the Flory equation for star macromolecules can be formulated as follows:

$$[\eta_\theta]_g = \Phi_\theta \frac{[\overline{R}^2_\theta]^{3/2}_g}{M} h^3. \qquad (3)$$

In 1953 Stockmayer and Fixmann [24,54] showed that the coefficient of friction of a branched macromolecule is related to the radius of inertia and the hydrodynamic radius:

$$F_{\theta g}/\eta_0 = \frac{\Phi^{1/3}_\theta}{2.5 \times 10^6} [\overline{R}^2_\theta]^{1/2} h, \qquad (4)$$

where $F_{\theta g}$ is the translational friction constant and

$$h^3 = [\eta_\theta]_g/[\eta_\theta]_l = f^{3/2}/[2 - f + \sqrt{2}\,(f-1)]. \qquad (5)$$

In this case $g^{1/2} < h^3 < g^{3/2}$.

Stockmayer and Fixmann [24,54] suggested that this relation remains valid for any branching model and can be used to find the functionality and the number of branching nodes, provided that the ratio $[\eta\theta]_g/[\eta\theta]_l$ is known.

However, Zimm and Kilb showed subsequently [55,61] that neither Eqn. (2) nor Eqns. (4) and (5) can be used with adequate reliability for the description of the behaviour of any star macromolecule in solution.

Zimm and Kilb [55,61] based their calculations on the model of a star molecule with f branches and N subchains, the centres of hydrodynamic interactions being located at the ends of the subchains. Zimm and Kilb examined two models of macromolecules with star branching: comprising one branching centre with four branches of equal length and one branching centre with two long and eight short branches. It was shown that the influence of branching on the hydrodynamic properties of macromolecules is somewhat smaller than on the size of the coil [22,26,55,62-64]. The increase of the hydrodynamic interaction factor only partly compensates the influence of the "contraction"† of the coils owing to branching on the hydrodynamic properties. The value of Φ for branched polymers exceeds by a factor of 6–27 that for linear polymers [2,65,66]. For this reason, Eqn. (4) is not rigorously justified, since the coefficient of friction and the viscosity, on which it is based, depend in different ways on the details of the structure of the macromolecule [23].

All this was taken into account in the studies of Zimm and Kilb [55,64], who showed that

$$[\eta_\theta]_g/[\eta_\theta]_l = g^{1/2},$$

for star macromolecules and

$$[\eta_\theta]_l/[\eta_\theta]_g \simeq \sqrt{3}.$$

Zimm and Kilb suggest that these equations can be applied with adequate approximation to any types of branched macromolecules [55,61]. However, it has been stated [61] that the Stockmayer–Fixmann and Zimm–Kilb calculations have been carried out for star macromolecules and that the *a priori* extension of the results to comb macromolecules is not always correct. Thus Kurata and Fukatsu [67] showed that, for statistically branched polymers, the ratio P_g/P_l, where $P \simeq \Phi^{1/2}/2.5 \times 10^6$, increases monotonically with increase of branching density, tending asymptotically to 1.34. For graft comb polymers, the ratio P_g/P_l initially increases with increasing branching density, passes through a maximum, and then falls, tending to unity regardless of the functionality of the branching. These results show that, in translational motion of macromolecules, the effective hydrodynamic dimensions depend not only on the density but also on the type of branching. Stockmayer and Fixmann [54,61] suggest that the effective hydrodynamic dimensions are the same in translational and rotational motion.

III. COMB MACROMOLECULES

1. Comb Homopolymers

Homopolymers with a comb macromolecular structure should be formally assigned to the class of linear polymers, since the length of the side branches is much smaller than the length of the main chain [32,68]. However, many specific properties make it necessary to treat comb polymers as a special type of branched polymer. Thus mainly orientation short-range order obtains in linear polymers and is to an overwhelming extent one-dimensional with a symmetry axis parallel to the molecular axis. In

† It is understood that the term "contraction" does not imply that the macromolecule actually contracts. The effective volume of the branched macromolecule is simply smaller than that of its linear analogue having the same molecular weight.

comb homopolymers, there is a possibility of two-dimensional order due to the intramolecular interaction of the long side branches and the intermolecular interaction between the main chains. Comb macromolecules tend to become ordered as a result of the association of the side chains, which is the reason for the ease of formation of ribbon structures[32,68]. Even in amorphous polymers with short side branches, order is observed, entailing the appearance of layer structures. The interaction of methylene chains in homopolymeric comb macromolecules has a decisive influence on the type of crystallisation, but the degree of ideality of the packing depends in many ways on the nature of the main chain[32,68]. An increase of the length of the side groups in comb homopolymers leads to an increase of the equilibrium rigidity of both the main chain of the macromolecule and of its side groups. This was demonstrated in a study of the behaviour of poly(methyl acrylate), poly(butyl acrylate), poly(octyl acrylate), and poly(octadecyl acrylate) in solution[37]. With increase of length of the side branches, the number of coiled conformations and the conformational stability of the macromolecules in solution increase[35].

It has been found for poly(cetyl methacrylate) that the length of the Kuhn segment is $A = 43$ Å.[34] This value exceeds by a factor of two the segmental dimensions of the majority of flexible chain molecules without complex side groups. It has been concluded[34] that the side chains of poly(cetyl methacrylate) molecules possess a high equilibrium rigidity and that there is an intramolecular orientation order in this polymer, exceeding the orientation order of Gaussian chains.

On the basis of the results of X-ray diffraction analysis of poly(hexadecyl acrylate) and poly(hexadecyl methacrylate), Shibaev and coworkers[33] showed that the side branches of poly(alkyl acrylates) and poly(alkyl methacrylates) in which the length of the side chains corresponds to ten and more carbon atoms form two-layer and one-layer types of hexagonal packing. The critical length of the side chain, equivalent to 9–10 carbon atoms, corresponds to the transition from the helical conformation of the macromolecules to layer structures with hexagonal packing of the side branches[32,68].

With increase of the length of the side chains in comb homopolymers [poly(phenyl methacrylate) and poly(chlorophenyl methacrylate)], the segmental anisotropy of the molecules becomes more pronounced, which can also be attributed to the influence of the interaction of the side groups, which becomes more intense with increase of their size[28].

2. Comb Heteropolymers (Copolymers)

In a study of the graft copolymers of poly(methyl methacrylate) and poly(butyl methacrylate) with polystyrene, which are distinguished by a high frequency of grafts and long main and side chains, it was shown[43] that, in all cases the hydrodynamic dimensions of the macromolecules of the graft comb copolymers in the same solvent are much smaller than those of the macromolecules of its constituent homopolymers having the same molecular weight (Fig. 2). However, the persistent chain length a, for example in the graft copolymer, is 50 Å, and the ratio $P = a/d = 1.8$, i.e. the macromolecules are rigid [d is the diameter (thickness) of the macromolecule].

Studies by Birshtein and coworkers[69] have shown that comb homo- and hetero-polymers should be regarded as pseudorigid (see Table). The persistent length $a = [\overline{h^2_\theta}]/2L$ characterises the degree of coiling or the equilibrium flexibility of the polymer chain. In the absence of bulk-phase interactions (at the θ-point), the statistical properties of polymer chains are determined mainly by the flexibility parameters a (or the length of the Kuhn segment $A = 2a$) and the relative dimensions L/a. However, many important properties of polymer chains are influenced by the interactions not only along but also across the chain. These include the degree of foldability, the arrangement of polymers in the amorphous and crystalline states, the extent and nature of the bulk-phase interactions between the macromolecules in solution, etc. The above characteristics depend not only on the length of the rigid section but also on its thickness or, more precisely, on the relative quantity a/d characterising the degree of extention of an individual persistent section of the chain (a/d is the parameter of the local asymmetry of the macromolecule[69]).

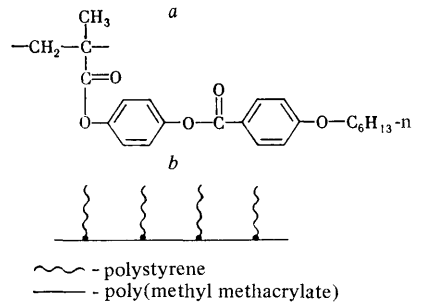


Figure 2. Comb macromolecules: *a*) comb homopolymers[29]; *b*) graft comb copolymers.

The main characteristic of pseudorigid polymers is large transverse dimensions of the chain. In the absence of a thick shell, the backbone of such pseudorigid comb macromolecules is appreciably flexible. However, when the chain is thick, the flexibility cannot be realised: the persistent length, i.e. the length of the section along which the chain bends, evidently cannot be smaller than its thickness. Therefore, for "thick" comb polymers of this kind, one must assume that $d \simeq a$, so that $a/d \simeq 1$. Thus pseudorigid macromolecules are characterised by a high value of a for a small local asymmetry[69]. In essence, pseudorigid molecules constitute to some extent an analogue of flexible molecules magnified severalfold: the scale factor a varies, but, for fixed relative dimensions L/a and a/d, the physical picture remains unaltered[69].

However, polymers with long side groups can be justifiably regarded as similar to the usual flexible but short chains only when the frequency of the distribution of side groups is fairly high. Otherwise, the differences between the chemical natures of the side groups and the chain backbone will have an effect. The microstructure of the section through a macromolecule with long side groups is determined primarily by the properties of the side chains, in particular by their intrinsic local asymmetry[69].

Furthermore, in contrast to linear macromolecules, the long-range interactions in graft comb copolymers (as in uniformly branched macromolecules[21]) are intense, which leads to very considerable (but virtually isotropic) swelling of the macromolecules in effective solvents[48].

Types of polymers with different local asymmetry[69].

Class of polymer	Polymer	d, Å	a, Å	a/d
Flexible	Polystyrene	10	9	~1.0
	Polyethylene	4	6	1.5
Rigid	Trinitrocellulose	8.3	100	~10
	Polyphenylsilsesquioxane	7	70	10
	Poly(butyl isocyanate)	8	500	~60
Pseudorigid	Poly(n-alkyl acrylates)	40	40	1
	Poly(methyl methacrylate)–polystyrene grafted copolymers	40	40	1

If the main chains of graft comb copolymers are capable of crystallisation and the side chains consist of irregular macromolecules (or conversely), then X-ray diffraction data suggest that order should persist in such a polymer even in the presence of a high content of the amorphous component[46].

It has been shown[53,56–60,70] that the theory of the worm-like chain is applicable to the description of the behaviour in solution of heteropolymeric comb macromolecules with short branches ($L_b \ll L_s$ and $l_b > L$). The rigidity of the main chain of such comb macromolecules proved to be much greater than that of the macromolecules of the corresponding homopolymers, since in graft macromolecules of this kind the conformation of the side chain is similar to that of a slightly bent rod. A unique combination of the considerable rigidity of the coil with its virtual impenetrability by the solvent has been observed, which is due to the large hydrodynamic (effective) diameter of such a worm-like chain.

IV. CHARACTERISTICS OF THE BEHAVIOUR IN SOLUTION OF STAR AND COMB MACROMOLECULES

1. Non-Gaussian Chains

Linear macromolecules in thermodynamically ideal solutions can be regarded as impenetrable coils with a Gaussian distribution of the segments relative to the centre of gravity. Branching leads to compacting of the segments and their more uniform distribution in the bulk of the macromolecule. Conformational statistics of a branched molecule can therefore be non-Gaussian even in an ideal solvent[61,71,72].

The dimensions of star and comb macromolecules depend both on the lengths of the branch and the backbone (L_v and L_s) and on the number of branches[73,74]. The comb macromolecule is characterised by the number of segments N_b belonging to a single branch and the number of segments N_s constituting the backbone of the macromolecule. For small values of N_b, the star molecule ceases to be a Gaussian coil and the same happens in the case of the comb macromolecule for small values of N_b and N_s.

Calculation of the branching factor g for star and comb macromolecules showed that, when N_s and $N_b \geq 100$, then the macromolecule is a Gaussian coil in a θ-solvent. Knowing the values of g for such macromolecules, it is possible to calculate the number of branches using tabulated data[55,56,67,73,75]. When $N_b < 100$, the branches of the star macromolecule become non-Gaussian. The factor g then diminishes with decrease of the number of segments in the branch. For example, when $f = 8$ and $N_b = 0.1$, 10, and 100, then $g = 0.075$, 0.325, and 0.340 respectively.

A similar dependence has been observed for comb macromolecules: for $f = 100$ and the ratio $N_b/N_s = 0.1$, we have $g = 0.038$ for $N_s = 1$ and $g = 0.114$ for $N_s = 100$. Thus the greater the rigidity of the backbone, the smaller the factor g.[73]

The radius of inertia of unperturbed star macromolecules is characterised by the relation[3]

$$[\bar{R}_0^2]_q = \frac{N_b A^2}{6}\left(\frac{3f-2}{f}\right), \tag{6}$$

the corresponding relation for comb macromolecules being

$$[\bar{R}_0^2]_g = \frac{A^2}{6}\left[N_s + 3N_b\frac{r}{1+r}\right], \tag{7}$$

where $r = N_b/l$.

On the other hand, if the branched macromolecule does not obey Gaussian statistics, the factor g must be estimated by comparing the dimensions of macromolecules having not only the same molecular weights but also the same thermodynamic rigidities, i.e. $A_g = A_l$. One must bear in mind that the thermodynamic rigidities of the main and side chains of a branched macromolecule are the same[21].

On the other hand, when $A_g \neq A_l$, the experimental factor g_e is related to the calculated factor g_t in the following way:

$$g_e = g_t\frac{A_g\left[1-\frac{3A_g}{2L}+\frac{3A_g^2}{2L^2}-\frac{3A_g^3}{4L^3}\left(1-e^{-\frac{2L}{A_g}}\right)\right]}{A_l\left[1-\frac{3A_l}{2L}+\frac{3A_l^2}{2L^2}-\frac{3A_l^3}{4L^3}\left(1-e^{-\frac{2L}{A_g}}\right)\right]}. \tag{8}$$

For a Gaussian chain, Eqn. (8) is converted into the relation $g_e = g_t A_b/Al$.

For a non-Gaussian star macromolecule, in which the chains are randomly oriented, the branching factor g_t is related to the number of branches f and the number of segments N_b in one branch[21]:

$$g_t = \frac{1}{Bf}\left\{6f\left[\frac{1}{6}-\frac{1}{4N_b}+\frac{1}{4N_b^2}-\frac{(1-e^{-2N_b})}{8N_b^3}-3f(f-1)\right]\times\right.$$
$$\left.\times\left[1-\frac{1}{2N_b}+\frac{(1-e^{-2N_b})^2}{8N_b^2}\right]\right\}, \tag{9}$$

where

$$B = 1-\frac{3}{2N_b f}+\frac{3}{2N_b^2 f^2}-\frac{3}{4N_b^3 f^3}(1-e^{-2fN_b}).$$

When $N_b > 100$, the relation is converted into the familiar relation for Gaussian branched macromolecules:

$$g_t = \frac{3f-2}{f^2}. \tag{10}$$

For regularly branched non-Gaussian comb macromolecules, in which the main and side chains have the same thermodynamic rigidities, the branching factor g_t is related to $\gamma = L_b/L_s$ and f in a very complex manner[21].

For Gaussian chains ($N_S > 100$, $\gamma N_S > 100$), g_t becomes

$$g_t = \left\{1 + \frac{\gamma f}{f+1}[(2f+1+3\gamma(f+1)] + \gamma^2 f(f-1)(1+3\gamma) + f\gamma^3\right\}(1+\gamma f)^{-3}. \quad (11)$$

If the main chain is Gaussian and the side chains are rigid rods, the[21] g_t becomes[12]

$$g_t = \frac{1}{(1+\gamma f)^3}\left\{1 + \frac{\gamma f}{f+1}[2f+1+\gamma(f+1)\ (2\gamma N_s+1)] + \right. \quad (12)$$
$$\left. + \gamma^2 f(f-1)(1+\gamma^2 N_s+\gamma) + \frac{f\gamma^3}{2}(\gamma N_s - 1)\right\}.$$

These equations are applicable to the estimation of the rigidities of comb homopolymers and graft comb copolymers. The factor g can be used to estimate quantitatively the degree of branching of the polymer. On comparing these results with those of Thurmond and Zimm[76], Kilb[64] and subsequently Kotlyar[77,78] and other workers[13,22] showed that the ratio of the intrinsic viscosities is a sufficiently reliable measure of the degree of branching:

$$g^{1/2} = [\eta_\theta]_g/[\eta_\theta]_l \cong [\eta]_g/[\eta]_l \cong g^n, \quad (13)$$

where g^i is the degree of branching of an impenetrable macromolecule. This ratio varies with the solvent used. However, the estimate of $[\eta\theta]_g$ must be treated critically and the use of very effective solvents must be avoided[25,79,80], since

$$[\eta]_g/[\eta]_l > [\eta_\theta]_g/[\eta_\theta]_l,$$

the discrepancy being greater the more effective solvent and the higher the molecular weight of the polymer.

The knowledge of the factor g_e makes it possible to determine with an adequate approximation the parameter f—the functionality of each point, provided that the number of branching points m is known. For star polymers with one, two, and three branching points, we have[22]

$$g_\theta^2 = \begin{cases}(3f-2)/f^2 & \text{when } m=1\\ (18f^2-28f+11)/(2f-1)^2 & \text{when } m=2\\ (51f^2-90f+40)/(3f-2)^3 & \text{when } m=3\end{cases}. \quad (14)$$

Knowing f, it is possible to determine in turn the number of branching points m[55,67]:

$$g^i = \begin{cases}\left[\left(1+\frac{m}{7}\right)^{1/2}+\frac{4m}{9\pi}\right]^{-1/4} & \text{when } f=3\\ \left[\left(1+\frac{m}{6}\right)^{1/2}+\frac{4m}{9\pi}\right]^{-1/4} & \text{when } f=4.\end{cases} \quad (15)$$

All the above values have been tabulated[55,67,75]. When the lengths of the branches in the macromolecule are not the same and there is a possibility of both long and short chains, Eqn. (15) becomes[81,82]

$$g_\theta^i = \frac{1}{m+1}[1+m(1-2f+2f^2-2f^3)+m^2(f+4f^2-4f^3)]. \quad (16)$$

2. The Degree of Branching and Swelling of Macromolecules

Another distinctive feature of branched macromolecules, particularly star and comb macromolecules, is as follows: under non-ideal conditions, the swelling of the macromolecular coil influences its size in opposition to the change in size caused by branching. The influence of the degree of branching is opposed to the influence of bulk-phase effects in effective solvents, where the segments are "diluted" in the bulk of the macromolecule[22,26,61,63].

Ptitsyn and Kron[22] showed that the bulk-phase effects influence the dimensions of the branched chains (the volume of the coil) much more than the dimensions of the corresponding linear chains, i.e. the nature of the excluded volume is determined by the probability of intramolecular contacts between the units in the coil. Furthermore, they showed[4,22] that the coefficient of volume expansion of a star molecule is a complex function:

$$\alpha_g^2 = \bar{R}_g^2/\bar{R}_{\theta g}^2 = 1 + \frac{134}{105}\chi z;\ z = \left(\frac{3}{2\pi}\right)^{3/2}\frac{N^{1/2}v}{6}. \quad (17)$$

For α_g close to unity, we have

$$\alpha_g^2 = 1 + \frac{134}{105}\frac{z}{g_\theta^3} + \ldots,$$

so that $\chi = 1/g_\theta^3$. For linear chains, $\chi = 1$. Ptitsyn and Kron[22] showed that Eqn. (17) is applicable only in the vicinity of the θ-point, where the bulk-phase effects are small. For large values of α_g, the equation for the swelling of branched macromolecules is analogous to Flory's equation for the swelling of a linear coil:

$$\alpha^5 - \alpha^3 = \frac{134}{105}\chi z. \quad (18)$$

Then we have $\bar{R}_g^2 \sim g_\theta^{4/5}$ when $\alpha \gg 1$, while $\bar{R}_{\theta g}^2 \sim g_\theta^2$, i.e. the bulk-phase effects partly compensate the decrease in the size of the macromolecule due to branching (the star shape).

When $\alpha \gg 1$, we have $\alpha_g = \alpha_l \chi^{1/3}$, whence

$$g \equiv [\bar{R}_g^2/\bar{R}_l^2]^{1/2} = g_\theta \frac{\alpha_g}{\alpha_l} \simeq g_\theta \chi^{1/2}. \quad (19)$$

Since $\chi \simeq \mu/g_\theta^3$, it follows that $g = \mu^{1/3}$. The parameter μ depends on the type of branching model and increases with increase of m. For high degrees of branching, $g \simeq \mu^{1/3}$, i.e. the ratio of the sizes of the branched and linear macromolecules with the same molecular weights tends to a constant value in an effective solvent as f increases, while in a θ-solvent it tends to zero[22].

The factor g_θ can decrease rapidly with increase of the molecular weight[22], which leads to a weaker dependence of $\bar{R}_{\theta g}^2$ on M for branched chains than for linear chains. Consequently the sizes of macromolecules in effective solvents, characterised by $[\bar{R}_g^2]^{1/2}$, are relatively insensitive to the degree of branching and cannot be used together with the ratio $\bar{R}_{\theta g}^2/M$ for the quantitative estimation of the degree of branching.

3. The θ-Temperatures

The third distinctive feature of star and comb polymers was noted in studies by Benoit and coworkers[3,4]. Whereas the equation for the swelling of a linear polymer in effective solvents is

$$\alpha^5 - \alpha^3 = 2C_{ml}\psi_1(1-\theta/T)M^{1/2}, \quad (20)$$

where the coefficient C_m for a given polymer and solvent is independent of the molecular weight of the polymer, for branched polymers Eqn. (20) assumes the following form:

$$\alpha^5 - \alpha^3 = 2C_{ml}\psi_1(1-\theta/T)M^{1/2}g^{3/2} + \left(\frac{2}{3}\right)\frac{C_{ml}}{\alpha^3}g^{-3}. \quad (21)$$

In this case $g = [\bar{R}_\theta^2]_g/[\bar{R}_\theta^2]_l$. The swelling coefficient α increases slowly with increasing molecular weight and depends on the properties of the solvent, the dependence

being more pronounced the higher the value of $\psi_1(1 - \theta/T)$, i.e. the more effective the solvent. When $T = \theta$, $\alpha = 1$.

Eqn. (21) shows that the swelling coefficient α for branched polymers (particularly for comb and star polymers) is not unity when $T = \theta$.[3,4] If the temperature at which $\alpha = 1$ is designated by θ_α. Eqn. (21) can be formulated thus:

$$\frac{\theta}{\theta_\alpha} - 1 = \frac{C_{ml} g^{-1/2}}{3 C_{ml} \psi_1 M^{1/2}}. \qquad (22)$$

According to this expression, the decrease in the molecular weight of the polymer or the increase in the reduced ratio results in a deviation of θ_α from Flory's θ-point. θ_α is always greater than θ and becomes equal to θ only when $M \to \infty$.

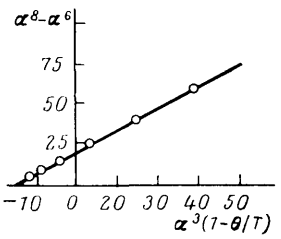


Figure 3. Determination of the θ-temperature by extrapolating a plot of $\alpha^8 - \alpha^6$ against $1 - \theta/T$ for star and comb polymers[3].

If the expansion (swelling) factor of the macromolecule α is designated by α_θ at Flory's temperature, Eqn. (21) can be written as follows:

$$\alpha_\theta^8 - \alpha_\theta^6 = \frac{2}{3} C_{ml} \cdot g^{-3}, \qquad (23)$$

i.e. α_θ is independent of M, depending only on g.

On the basis of the foregoing, one should consider two temperatures: one at which $A_2 = 0$, i.e. θ_{A_2} and the other, Flory's θ-temperature, at which A_2 is not zero, i.e. is equal to $A_{2\theta}$. Incidentally θ_{A_2} does not differ very significantly from the θ-temperature‡. Thus one may speak of the existence of two characteristic temperatures for star and comb polymers, namely the θ_α temperature at which $\alpha = 1$ and θ_{A_2}, the temperature at which $A_2 = 0$. Both temperatures differ from Flory's classical§ θ-temperature, and the relation[3,4]

$$\theta_\alpha < \theta_{A_2} < \theta$$

holds most frequently.

However, Vrii[83] and Casassa[84] claim that the relation $\theta_\alpha < \theta < \theta_{A_2}$ is valid.

In order to find θ_α (and hence $\bar{R}^2_{\theta g}$), the sizes of the branched macromolecules are determined in any solvent at different temperatures and plots of the type shown in Figs. 3 and 4 are constructed[3,4].

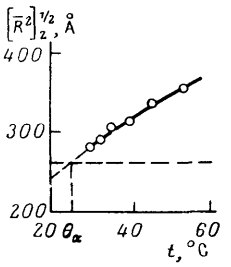


Figure 4. Determination of the θ-temperatures for star and comb polymers from the variation of $[\bar{R}^2]_z^{1/2}$ with increasing temperature of the solution[3].

The swelling factors α_R for star and comb polymers are equal[4,83,85]:

$$\alpha_{Rg}^2 = \bar{R}^2_{\theta g} / \bar{R}^2_{\theta r}.$$

The viscometric coefficient of expansion for polymers with randomly branched macromolecules and star macromolecules α_η is given correspondingly by the expressions

$$\alpha_{\eta g^*} = [\eta]_{g^*} / [\eta_\theta]_{g^*}; \quad \alpha_{\eta g} = [\eta]_g / [\eta_\theta]_g.$$

The relation between $\alpha_{\eta g^*}$ and $\alpha_{\eta g}$ can be formulated as follows:

$$\alpha^3_{\eta g^*} - 1 = \frac{3}{2}(\alpha^3_{\eta g} - 1). \qquad (24)$$

The relations between $\alpha^3_{\eta g} - 1$ and $(1 - \theta/T)M^{1/2}$ and between $\alpha_{\eta g^*}$ and $\alpha_{\eta g}$ are linear for branched polymers with different functionalities (Figs. 5 and 6). Fig. 6 shows that $\alpha_{\eta g}$ for star macromolecules is always greater than for randomly branched macromolecules[5].

‡ In order to avoid terminological and semantic confusion, we may note that, according to Flory, the only sign of the θ-state, i.e. of the pseudoideality of the solution, is not the equality of the swelling parameter α to unity, but the equality of the second virial coefficient to zero. This should be remembered in considering θ-points with different subscripts.

§ When $\alpha = 1$ and $A_2 = 0$ simultaneously.

4. Dependence of $[\eta]$ on M

The degree of branching of macromolecules is reflected in the nature of the dependence of $[\eta]$ on M.[24,55,63,75,76,86-89] The plot of $\lg[\eta]$ against $\lg M$ for cascade polymers may become curved in the presence of macromolecules with different degrees of branching and the greater the increase of the degree of branching with increasing molecular weight of the polymer the smaller the value of a and the larger the value of K in the Mark-Kuhn-Houwink equation [Eqn.(25)]:

$$[\eta]=K_\eta M^{a-\varphi};\ S_0=K_s M^{1-b}\equiv K_s M^{1-\left(\frac{a-\varphi+1}{3}\right)}=K_s M^{1-\left(b-\frac{\varphi}{3}\right)}. \quad (25)$$

The relation $b = (a + 1)/3$ holds for branched polymers.

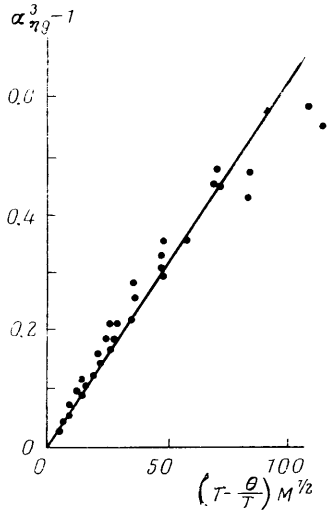


Figure 5. Increase of the swelling coefficient of star polystyrene with $(1 - \theta/T)M^{1/2}$.

Zimm and Stockmayer[50] showed that a can vary as follows with the degree of branching:

$$a_g=a_l+(2-a_l)\frac{d\ln g}{d\ln P}. \quad (26)$$

Since $d \ln g/d \ln P < 0$, we have $a_g < a_l$.

According to Zimm and Kilb[55,75], for a high degree of branching in effective solvents, Eqn.(25) becomes

$$[\eta]=K_\eta M^{a-0.25}, \quad (27a)$$

while in a θ-solvent we have

$$[\eta]_{\theta g}=K_\theta\cdot M^{0.25}. \quad (27b)$$

Thus the parameter a in Eqn.(25) is always smaller for branched polymers than for linear polymers (star polymers are an exception). In a θ-solvent, the parameter becomes equal to 0.25, in contrast to 0.5 for linear polymers.

The dependence of the parameter $g^i = [\eta_\theta]_g/[\eta_\theta]_l$ on M is determined by the dependence of the number of branching units m on M. For single-centre star macromolecules, the factor m is independent of M.

As early as 1948, Flory showed that the parameter a in Eqn.(25) for star molecules with $f = 1$, **2**, or 3 is the same as the value of a for linear macromolecules. Flory observed the variation of a only with increase of f (for f = 8), which can probably be explained by the breakdown of the star properties.

It has been shown[52] for star polystyrene that the parameters a and the swelling factors α^3_η for linear and star polystyrenes are identical. The parameter a remains constant even in solvents which are not θ-solvents.

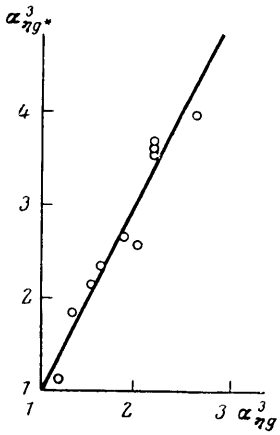


Figure 6. Relative change in the viscometric swelling coefficient of star ($\alpha^3_{\eta g}$) and randomly branched ($\alpha^3_{\eta g*}$) polystyrene[5].

For polymers with the comb structure of macromolecules, the dependence of $[\eta]$ on M is different[90-93]. As noted above, a characteristic feature of a comb macromolecule is the great rigidity of its main chain accompanied by an appreciable density in the distribution of segments in the part of the volume adjoining the main chain (owing to the branches)[53,56-60]. As noted by Tsvetkov and coworkers[70,90,94] the best model for the description of the hydrodynamic properties of such a molecule is a wormlike chain, the main parameters of which are the contour length L, the hydrodynamic diameter d, and the persistent length a (formally equal to half the statistical Kuhn segment A).

The use of the worm-like chain model, the viscosity data, and data for translational and rotational friction can yield reliable data on the conformational characteristics of the macromolecules of comb heteropolymers[93]. As for rigid-chain polymers, the sizes of the macromolecules of comb polymers vary little with the solvent, which makes it possible to neglect the influence of bulk-phase effects on their conformational properties[93].

A characteristic feature of many comb copolymers is their relatively low intrinsic viscosity compared with that of the linear homopolymer having the same structure as the main chain of the comb copolymer and the same molecular weight. This led some investigators to the idea of a globular structure of the molecules of comb copolymers. However, in reality the hydrodynamic properties of comb copolymers are fully consistent with those of a linear worm-like chain[93].

The value $a = 0.5$ in Eqn. (25) is not limiting for comb copolymers. We have[93]

$$M/[\eta] = \frac{1}{0.43\,N_A}(M/LA)^{3/2}M^{1/2} = \left(\frac{2.3\lg A}{d} - 1.6\right)\cdot\frac{M^2}{L^2}\cdot\frac{1}{A}. \quad (28)$$

For a fairly large diameter of the macromolecule ($d > 0.2$ Å), the dependence of $M/[\eta]$ on $\sqrt{M}$ can be represented by a straight line, which makes a negative intercept on the ordinate axis. With increase of M, the intrinsic viscosity $[\eta]$ evidently increases more slowly than does $M^{0.5}$, i.e. we have $a < 0.5$ depending on $[\eta] = KM^a$. This case has been examined (for $S = 33$).[93,94]

If the structure of the chain of a comb copolymer corresponds to the condition $A/d \simeq 1$, it follows from Eqn. (28) and the expression[93]

$$S_s = A/\lambda = \frac{M_0}{\lambda^2(1-x_1)}\cdot(0.43\,N_A\,d\,y/dz)^{-3/2} \quad (29)$$

(where x_0 is the mole fraction of component B forming the branches of the comb macromolecule) that

$$S_s = [M_0[\eta]/0.43\,N_A P^{1/2}(1-x_0)]^{-2/3}\lambda^{-2}. \quad (30)$$

Eqn. (30) shows that the rigidity of the main chain of the comb macromolecule may be determined directly from the intrinsic viscosity[93].

It must be emphasised again that the cause of the great rigidity and order of the macromolecules of comb copolymers investigated[53,56-60,90,94] should be sought in the interaction of the branches. These interactions lead to the formation of intramolecular structures with a high degree of orientation order. Such structures may be a consequence of the strong dispersion interaction of the polystyrene chains constituting the branches of graft comb macromolecules. Relations of this kind have been traced for the homologous series of graft comb copolymers of poly(methyl methacrylate) with styrene, the contour length of the main chain of which L varies from 9000 to 3700 Å.[90,93]

A rare instance (see Table) of comb copolymers [grafted copolymers of poly(methyl methacrylate) with styrene] whose contour length L is comparable to their persistent length has been examined[90]. Low values of the exponential coefficients a and b ($a < 0.5$) have been noted for such copolymers: $[\eta] = 0.11\times10^{-4}M^{0.43}$ and $S_0 = 1.2\times10^{-15}M^{0.54}$. In this case, the contour length of the macromolecule L is modelled by a persistent chain with a contour length L equal to the length of the main chain of poly(methyl methacrylate):

$$L = \frac{M(1-x_1)\lambda}{M_0}, \quad (31)$$

where M_0 is the molecular weight of the monomer unit of the main chain.

In conclusion of the discussion of comb macromolecules, we emphasise yet again that the different "anomalies" in their properties compared with their linear analogues or homologues can be due to three different causes, linked directly with the configuration (structure) of the macromolecules.

1. In comb homopolymers, more than 80% of the molecular weight is as a rule contained in the branches. Depending on the structure of these branches, gel formation may begin already at low concentrations, regardless of the degree of stereoregularity, owing to the crystallisation of sections of the branches or, according to Tsvetkov[29], a long-range order, similar to that in liquid crystals, may arise within the chains. The first version is characteristic of poly(alkyl acrylates) or poly(alkyl methacrylates) and the second is characteristic of polymers whose side groups are capable of forming thermotropic or lyotropic liquid crystals in the "free state".

These anomalies in the two versions persist for a fairly long time also on diluting the "long-chain" units by short-chain units (for example, methyl methacrylate or acrylate units), i.e. on passing from a comb homopolymer to a statistical comb copolymer with infrequent long side chains. However, after the attainment of a "critical" dilution, the effects of intrachain and interchain ordering, leading to "anomalies", vanish.

2. In comb heteropolymers, i.e. in graft copolymers, the anomalies arise from segregation effects due to the different natures of the backbone chain and the branches¶. The hydrodynamic (but not thermodynamic!) behaviour of such macromolecules is simulated by a "thick" impenetrable worm-like chain.

3. In "classical" branched comb homopolymers, there are no longer any selective effects; however, the increased density in the distribution of segments—a direct consequence of branching—leads to a decrease ("slight contraction") of the hydrodynamic volume of the macromolecules and hence to a change in the "normal" parameters in Eqns. (25) for the intrinsic viscosity and the translational friction constant.

V. THE INFLUENCE OF POLYDISPERSITY ON THE BRANCHING PARAMETERS

The branching parameters of macromolecules are influenced significantly not only by the type of branching and the length and frequency of the branches, but also by parameters such as the molecular weights, the polydispersities of the main and side chains, and the distribution of branches with respect to molecular weight. This is manifested particularly clearly in the study of long-chain branching[1,95-101].

The number-average molecular weight of a branched macromolecule with f branches varies as follows with the number of branches relative to the molecular weight of a linear polymer having the same chemical composition[1,95,96]:

$$\overline{M}_{nf}/\overline{M}_{nl} = f. \quad (32)$$

The variation of f is associated solely with the number of branches regardless of their length. A higher-order molecular weight ($\overline{M}_w$, $\overline{M}_z$, etc.) is influenced also by the size of the chains. Comparison of different average molecular weights ($\overline{M}_n$, $\overline{M}_w$, $\overline{M}_z$) of branched and linear specimens therefore yields information not only about the number but also about the size of the branches. For example, the large change in $\overline{M}_n$ associated with a slight change in $\overline{M}_w$ indicates a large number of short branches.

¶See "Entsiklopediya Polimerov" (The Encyclopaedia of Polymers), Vol. II, "Makromolekula" (The Macromolecule).

Conversely, a small number of long branches (comparable in length to the main chain) leads to an appreciable decrease of $\bar{M}_w$ with a relatively slight change in $\bar{M}_n$.[95]

The knowledge of the average molecular weights of branched and linear polymers makes it possible to calculate other branching parameters. This was done by Budtov and coworkers[95,102] for the comb esters of poly(vinyl alcohol) with long-chain branching and by Burchard[103,104] for star polymers. Such branching parameters include the distribution of the branching centres among molecules with different molecular weights, the polydispersities of the branches and backbones with respect to length, and the average molecular weights of the centre of the star and its branches in the case where the centre has a chemical structure different from that of the branches (Fig. 1*b*).[103] Burchard showed that in the latter case the masses of the centre and of the star are given by the following expressions respectively:

$$m_c = \frac{(1-\beta)\bar{M}_{wc}}{\alpha f\bar{M}_{wg} + (1-\beta)\bar{M}_{wc}}\ ;\ m_g = \frac{\alpha f\bar{M}_{wg}}{\alpha f\bar{M}_{wg} + (1-\beta)\bar{M}_{wc}}\ . \qquad (33)$$

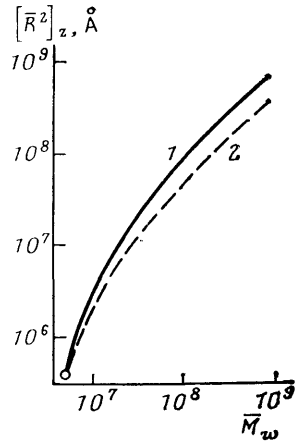


Figure 7. Variation of the mean square radius of inertia with increase of the molecular weight of a polyfunctional star macromolecule[97]: 1) polymer with the "most probable" distribution of branches; 2) monodisperse branches.

For a homodisperse centre, $\bar{M}_{nc} = \bar{M}_{wc}$; in the case of branches with the "most probable" distribution $\bar{M}_{ng} = \bar{M}_{wg}(1-\beta)$ ($\bar{M}_{ng}$, $\bar{M}_{nc}$, and $\bar{M}_{ns}$ are the number average molecular weights of the centre and branches of a star macromolecule respectively, $\bar{M}_{wg}$ is the weight-average molecular weight of the star macromolecule, and β is the probability of the interaction of the branches with one another). Evidently this equation is valid also for comb polymers.

The relations examined above were derived for a star macromolecule with polydisperse branches[103]. The mean square radii of inertia of star macromolecules with polydisperse and monodisperse branches are significantly different. This difference increases particularly markedly with increased molecular weight of the star polymer (Fig. 7). For the same functionality of branching, the factor g of star polymers depends on the polydispersity of the branches.

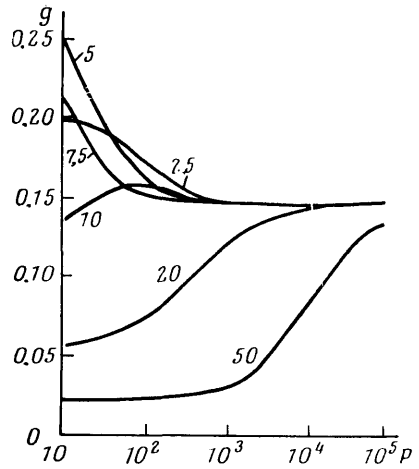


Figure 8. Variation of the factor g with increase of the degree of polymerisation for star macromolecules having a large centre[97]. The numerals against the curves represent the ratio l_c/l_s.

Fig. 8 shows that, for the "most probable" distribution with respect to the lengths of the branches ($\alpha = 1$), the value of g for a homodisperse star polymer is smaller than for a polydisperse star polymer. For the same degree of polymerisation of a star polymer P, the rigidity factor g of a star with a large centre depends significantly on the effective length of the bond l_c between two centres and the length of the bond l_s between two branches, as can be seen in Fig. 8. The average hydrodynamic radii of inertia of such polymers with polydisperse branches $[\bar{R}^2]_z^{1/2}$ vary in accordance with the following law[103]:

$$[\bar{R}^2]_{zl} = \frac{l_s^2}{4}\frac{\bar{M}_{wg}}{\bar{M}_s} = \frac{l_s^2}{4(1-\beta)}[2+(f-1)\alpha], \qquad (34)$$

where β is the probability of the interaction of the branches with one another.

For a polymer with monodisperse branches, we have

$$[\bar{R}^2]_{zl}^{1/2} = \frac{l_s^2}{6}\frac{\bar{M}_{wg}}{\bar{M}_s} = \frac{l_s^2}{6}N[1-(f-1)\alpha]. \qquad (35)$$

Thus the parameter g cannot be used by itself without a far-reaching study of other branching parameters, the molecular weight, and the molecular weight distribution of the polymer, its branches, and the centre of the macromolecule, with both star and comb structures[91,92].

Budtov and Godunova[102] proposed a method for the estimation of the polydispersities of the branches and backbones from the lengths for comb polymers and a method for estimating the distribution of branching nodes.

The following relations are valid for the number-average and weight-average molecular weights of comb polymers $\bar{M}_{ng}$ and $\bar{M}_{wg}$:

$$\bar{M}_{ng} = \bar{M}_{ns} + f_n\bar{M}_{nb} \qquad (36)$$

$$\bar{M}_{ng}\ \bar{M}_{wl} = \bar{M}_{ws}\ \bar{M}_{ns} + f_n\bar{M}_{bs}\bar{M}_{wb}, \qquad (37)$$

$$\bar{M}_{ng}\bar{M}_{wg} = \bar{M}_{ws}\bar{M}_{ns} + 2\bar{M}_{ns}B_{ws} + f_n\bar{M}_{bs}B_w,$$

where $\bar{M}_{ns}$, $\bar{M}_{ws}$, $\bar{M}_{nb}$, and $\bar{M}_{wb}$ are the number-average and weight-average molecular weights of the backbones and branches and f_n is the number-average number of branches per molecule,

$$B_w = \frac{\sum_i B_i^2}{\sum_i B_i}; \quad B_{ws} = \frac{\sum_i \bar{M}_{si} B_i}{\sum_i \bar{M}_{si}}, \tag{38}$$

(here $B_i = \Sigma_k f_{ik} \bar{M}_{bk}$ is the mass of all the branches of the ith molecule, and f_{ik} is the number of branches in the ith molecule with the molecular weight equal to $\bar{M}_{bk}$).

The branched structure is characterised by the polydispersity of the backbones and branches:

$$\alpha_s = \frac{\bar{M}_{ws}}{\bar{M}_{ns}}; \quad \alpha_b = \frac{\bar{M}_{wb}}{\bar{M}_{nb}}. \tag{39}$$

If

$$\bar{M}_{ns} \leq \bar{M}_{ng},$$

then

$$\bar{M}_{ns} = \frac{\bar{M}_{ng}}{\alpha_b/\alpha_s + f_n}\left[\frac{\alpha_b}{\alpha_s} + f_n\sqrt{\frac{\bar{M}_{wl}}{\alpha_s \bar{M}_{ng}} - \frac{\alpha_b}{\alpha_s f_n}\left(1 - \frac{\bar{M}_{wl}}{\alpha_s \bar{M}_{ng}}\right)}\right], \tag{40a}$$

$$\bar{M}_{nb} = \frac{\bar{M}_{ng}}{\alpha_b/\alpha_s + f_n}\left[1 - \sqrt{\frac{\bar{M}_{wl}}{\alpha_s \bar{M}_{ng}} \frac{\alpha_b}{\alpha_s f_n}\left(1 - \frac{\bar{M}_{wl}}{\alpha_s \bar{M}_{ng}}\right)}\right]. \tag{40b}$$

In all cases, $f_n = \bar{M}_{ng}/\bar{M}_{nl} - 1$. The limits of the variation of α_s and α_b may be as follows:

$$\alpha_s \geqslant \frac{\bar{M}_{wl}}{\bar{M}_{ng}}; \quad \alpha_b \leqslant f_n \cdot \frac{\bar{M}_{wl}/\bar{M}_{ng}}{1 - \bar{M}_{wl}/\alpha_s \bar{M}_{ng}}. \tag{41}$$

The lower limit of the polydispersity of the branches $\alpha_b \geqslant 1$ and the upper limit of the polydispersity of the backbone is defined by the condition

$$\alpha_s \leqslant \frac{\bar{M}_{wl}/\bar{M}_{ng}}{1 - f_n \bar{M}_{wl}/\bar{M}_{ng}}. \tag{42}$$

At the same time, the polydispersities of the backbones and branches, α_s and α_b, should be smaller than the polydispersities of linear and branched specimens:

$$\bar{M}_{wl}/\bar{M}_{ng} \leqslant \alpha_s; \quad 1 \leqslant \alpha_b \leqslant \bar{M}_{wl}/\bar{M}_{nl}. \tag{43}$$

The relations obtained are fairly general and make it possible to estimate reliably branching parameters such as $\bar{M}_{ns}$, $\bar{M}_{nb}$, α_s, and α_b.

If it is assumed that the mass of all the branches is smaller than that of the backbone, we obtained from Eqn. (38)[102]

$$B_{ws} \simeq \frac{\bar{M}_{ng} \cdot \bar{M}_{wg} - \bar{M}_{ws} \cdot \bar{M}_{ns}}{2\bar{M}_{ns}}, \tag{44}$$

which leads to yet another branching parameter:

$$f_{ws} = B_{ws}/\bar{M}_{wb}. \tag{45}$$

Substitution in Eqn. (45) of various model distribution functions and of the equations for the dependence of f_i and M_{B_i} on B_{S_i} leads to the conclusion that $f_{ws} \geqslant f_w$ (f_w is the number-average number of branches per molecule).

Comparison of f_n and f_{ws} permits a qualitative conclusion concerning the distribution of branching nodes among molecules having different molecular weights.

For a faster quantitative determination of the dependence of the branching parameters of star and comb polymers on their hydrodynamic properties and for the determination of molecular weights in the presence of long-chain branching, nomograms [97,103-106] and matrix methods [107] have been proposed in a number of studies.

The experimental studies carried out by Frenkel and coworkers [99-101] in order to test the influence of the polydispersity of the initial homopolymers on the final polydispersity of the graft comb copolymers showed that, for example, the molecular weight distribution (MWD) in a graft copolymer of cellulose with polyacrylonitrile and poly(methyl methacrylate) and the distribution of the molecular weights of polyacrylonitrile and poly(methyl methacrylate) as well as the cellulose chains is narrower than in homopolymerisation. The Schultz inhomogeneity parameter $U = \bar{M}_w/\bar{M}_n - 1$ varies from 0.25 to 0.57 under these conditions [101].

The study of the graft polymerisation of methyl methacrylate on wool [100] showed that the molecular weight distribution of the graft poly(methyl methacrylate) chains is unimodal and narrower than in free homopolymerisation.

Such narrowing of the molecular weight distribution of the chains compared with the free polymerisation of the monomer constituting the branches is due (other conditions being equal) to the same segregation effects which give rise to the anomalies in the hydrodynamic and thermodynamic behaviour of graft comb copolymers. Segregation occurs for high positive values of the thermodynamic parameter χ_{AB}, which can be treated, by analogy with the Flory–Huggins parameter χ_1, as the change in the free energy of the polymer A, playing the role of the "solvent", when a bound (in the chain of a second polymer) unit or segment of type B is introduced into it (or conversely). The theory of χ_{AB} is fairly complex and we cannot consider it here. However, it follows from it that the free energy of a macromolecule increases continuously as branches of another polymer grow on it. For this reason, a moment is inevitably reached when further growth of the branches become energetically unfavourable. This leads to a sharp increase of the chain termination rate constant or a decrease of the chain propagation rate constant or both simultaneously. Since the width of the molecular weight distribution is determined unambiguously by the ratio of the rate of termination r_t to the rate of propagation r_p, the normal distribution of the molecular weights of the branches must be

$$q_n(P) = \alpha(P)\, e^{-\int_1^P \alpha(P)\, dP}, \tag{46}$$

where $\alpha = r_t/r_p$ and P is the degree of polymerisation at any instant. Eqn. (46) shows immediately that, when $d\alpha/dP > 0$ (this happens precisely because of segregation and to a greater extent the higher the value of χ_{AB}), the statistical width of the molecular weight distribution, estimated from the ratio $\bar{P}_w/\bar{P}_n$, should diminish.

Graft polymerisation is frequently accompanied by the partial degradation of the chains on which grafting takes place; the equalisation of the molecular weight distribution can now proceed with respect to two parameters M_A and M_B. Some evidence for such equalisation has been obtained recently in the analysis of the grafting of acrylamide on cellulose [109].

VI. CONCLUSION

If we disregard three-dimensional polymerisation or polycondensation, the problem of the branching of macromolecules arose initially as a side effect in linear polymerisation at the expense of higher degrees of conversion when polymerisation is carried out under technological conditions.

The marked influence of branching on the set of physical characteristics and the practical properties of articles made of polymers required the development of analytical methods for the determination of the degree of branching, mainly in order to monitor the polymerisation process itself. However, the difficulty of direct linear analysis required the development of model concepts. Star and comb polymers cannot arise as a result of a random process. However, it is more convenient to carry out experiments with such polymers in order to test theoretical relations. Special syntheses of polymers of this kind were therefore undertaken and it was found that, in contrast to statistically branched polymers, they may possess "intrinsic useful properties", which is a situation characteristic of the development of the chemistry and physics of polymers at the present stage where research techniques are converted into applied methods and model compounds are converted into real materials (in a broad sense of the last term).

This applies particularly to two of the three types of comb polymers examined--capable of forming ordered (and regular) structures via their branches and of forming microheterogeneous "alloys" as a result of segregation (graft copolymers). Segregation has now found wide-scale applications in the industrial manufacture of impact-resistant polystyrene plastics.

The applications of star polymers are associated, in principle, with imparting catalytic functions to the latter.

The purely analytical aspect still retains its importance--in all cases where branching develops via a cascade mechanism it becomes uncontrollable and can lower significantly the useful characteristics of the polymer. Since, as in the case of the molecular weight distribution or the inhomogeneity of the composition of the copolymers, the quantitative branching characteristics reflect fine details of the kinetics and mechanism of the polymerisation or polycondensation, the study of these characteristics is not only of interest from the standpoint of "control" but is also of independent interest. (A completely up to date example is provided by the analysis of the side reactions in the formation of ladder polysiloxanes [110].)

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