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Degree of Branching in Polymeric Chains

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The degree of branching of polymeric chains is one of the most important molecular parameters which determine the physicomechanical and technological properties of the polymers.
The results of theoretical calculations of the influence of the degree of branching on the dimensions and nydrodynamic properties of the macromolecules are surveyed. The experimental results from the study of the properties and methods of synthesis of various model branched polymers are systematised. The problem of the molecular weight distribution of branched polymers and also experimental methods of determining the degree of branching of mono- and polydisperse polymers are considered briefly.

I. INTRODUCTION

The presence of branching in molecular chains leads to extensive changes in the physico-mechanical and technological properties of various polymers in comparison to the corresponding linear polymers. For example, branched divinylstyrene rubbers, polybutadienes, and other branched elastomers have less elasticity, lower breaking stress, etc.[1-4]; the decrease in the strength properties and the change in dynamical mechanical characteristics with increase in the degree of branching are characteristic also with such thermoplastic polymers as polystyrene, polyethylene, poly(vinyl chloride), etc.[5-7]. There are also significant differences in the rheological properties of linear and branched polymers. Thus at low loads (shear stresses) linear polymers and their melts flow like newtonian liquids and exhibit a viscosity lower than that of the branched polymers but under higher loads the flow departs from newtonian so that the viscosity of a branched polymer is less (or almost equal) to that of the linear[8,9]. Similar rules also hold for concentrated solutions. Hence like the regularity of the structure of the polymeric chains, the molecular weight, and the molecular weight distribution (MWD), the degree of branching is a most important molecular parameter of polymers. Branching arises during polymerisation mainly as a result of reactions in which active centres are transferred to the polymer chain; during this either the loss (abstraction) of a hydrogen atom in one of the monomeric units or the interaction of active centres with double bonds of the polymer chain is possible. In radical polymerisation these reactions take place in the following way:

1. Loss of a proton, H:

$$\sim M_n^{\cdot} + P_m \rightarrow M_nH + P_{m(-H)}^{\cdot};$$

$$\sim M_n^{\cdot} + \sim CH_2{-}CHR{-}CH_2 \sim \rightarrow M_nH + \sim CH_2{-}\dot{C}R{-}CH_2\sim$$

2. Interaction with the double bond:

$$\sim M_n^{\cdot} + P_m \rightarrow \sim M_{n+m}^{\cdot};$$

$$\sim M_n^{\cdot} + \sim CH=CH\sim \rightarrow \sim \overset{M_n}{\overset{|}{\dot{C}H}}{-}CH\sim.$$

Here $\sim M_n^{\cdot}$ and P_m denote the "live" and "dead" polymeric links of degree of polymerisation n and m respectively. (Two "live" polymeric chains can take part in the interaction but usually this is less probable.) In the first instance so-called trifunctional branching nodes are formed, in the second, tetrafunctional nodes (the branches leave from two points separated by a C–C bond and the distance between them can be neglected).

Similar changes also take place in catalytic polymerisation by the formation of branched molecules of different functionality. Clearly, not one but several branching nodes can be formed in a single macromolecule (but usually with fixed functionality).

Branched polymers with f-functional nodes are also formed in widely employed syntheses for the common polycondensation of bi- and f-functional monomeric units and in the irradiation of polymers.

II. FUNDAMENTAL CONCEPTS

In dependence on length, long-chain and short-chain branches are distinguished. Branches of a length commensurate with that of the main chain are termed long-chain, and the present article will mainly consider long-chain branching. By the length of a branch we understand the distance between the two nearest nodes of the branching or the distance between the nearest pair of nodes of the branching the end of the chain. Examples are distinguished when all the branches have the same length

(branching with a fixed chain length) and when there is a random distribution of branch lengths. This shows that if the structure of a branched molecule is determined by the molecular weight of each branch then any structures with a specified total number of nodes and molecular weight for the macromolecule are equally probable. Depending upon the nature of the attachment of the branches, branched molecules can be divided into: (1) comblike (graft branching), where the branches are attached to a main chain (Fig. 1*a*) and (2) statistical, where the polymer does not have a main chain (Fig. 1*b*); such structures can arise because of secondary branching†.

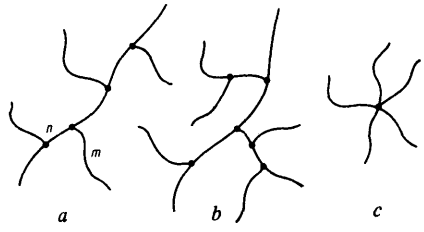


Figure 1. Models of branched macromolecules: *a*) comblike branched; *b*) statistically branched; *c*) starlike branched.

Whatever the nature of the branching the number of branches p is connected with the number of nodes b and the functionality of the branching by the relation:

$$p=(f-1)b+1. \quad (1)$$

A measure of the quantitative characteristic of branching is the branching density ρ, equal to the fraction of "cross-linked" (that is, having branching nodes) monomeric units in relation to their total number in the macromolecule:

$$\rho=\alpha\frac{b}{x} \quad (2)$$

where x is the degree of polymerisation, and α a constant depending on the functionality of the branching.

When during polymerisation the branching density exceeds some critical value ρ_c, which depends on molecular weight, an insoluble polymer starts to form, a gel which is a single space lattice [10,11]. Sometimes reference is made to the "degree of cross-linking" of polymeric molecules, characterised by the cross-linking (branching) parameter γ, where

$$\gamma=\rho/\rho_c \quad (3)$$

$\gamma = 1$ corresponds to the moment of gel formation.

III. UNPERTURBED DIMENSIONS OF BRANCHED MACROMOLECULES

In view of the small number of nodes in long-chain branching spectroscopic methods are used for identifying branched polymers. Therefore branching is investigated in dilute solutions, because the introduction of even one or two long-chain branching nodes leads to an appreciable decrease in the mean square dimensions of the macromolecules in comparison with linear ones of the same molecular weight.

The calculation of the undisturbed dimensions (that is, the dimensions in a θ-solvent) of branched macromolecules of various types has been carried out by various authors, who usually calculated the ratio of the mean square radii of inertia of branched $\overline{R}_b^2$ and linear $\overline{R}_l^2$ molecules of the same molecular weight; the g-factor is:

$$g=\overline{R}_b^2/\overline{R}_l^2. \quad (4)$$

For a small number of branching nodes this calculation can be made from purely geometric considerations. With a significant increase in the number of nodes statistical methods are employed. For example, for a branched macromolecule with one branching node a geometrical consideration gives [12]:

$$g=\sum_\lambda\left(\frac{3n_\lambda^2}{n^2}-\frac{2n_\lambda^3}{n^3}\right) \quad (5)$$

where n is the total number of segments (kinetically independent units) in the macromolecule), and n_λ the number of segments in the λ branch.

If a node has functionality f and the branch has a fixed length, that is, $n_\lambda = n/f$, then for such a star-shaped molecule we obtain from Eqn. (5):

$$g=\frac{3}{f}-\frac{2}{f^2} \quad (6)$$

in the particular example of trifunctional branching $g = 7/9$ and for tetrafunctional $g = 5/8$. For arbitrary branching the general equation for the g-factor has the form [13,14]:

$$g=\frac{6}{p(p+1)(p+2)}\left\{p^2+\sum_{\lambda,\mu}\nu_{\lambda\mu}\right\}. \quad (7)$$

Here $\nu_{\lambda\mu}$ is the number of branches between any two isolated branches λ and μ and the summation is over all the possible subdivisions of p branches of the macromolecule into different pairs (subsystems). Depending on the nature of the attachment of the branches and their distribution in lengths (at a given molecular weight and number of branching nodes) the sum will be somewhat different and the value of the g-factor will change correspondingly. From physical considerations it is evident that comblike branched macromolecules possess a large number of different subsystems compared with the statistically branched ones; fixing the branch lengths also leads to a decrease in the number of possible subsystems. Hence statistically branched macromolecules with a fixed branch length exhibit the least number of subsystems. The values of the g-factor should decrease in the same order. Accurate calculations have been made by Zimm and Stockmayer [12], Ptitsyn [15], and Kurata and Fukatsu [16].

In these studies values of the g-factor for various models of branching were calculated assuming that the branches are sufficiently long, that is, the distribution of the distances between the segments in the branches is a gaussian function. Table 1 gives the results of calculations [12,15,16] for various models of the branching. We note that the value of the g-factor for a given type of branching depends only on the number of branching nodes.

Tsvetkov developed an approximate method for calculating the dimensions of a branched chain in which the length of a side branch equals the length of the main chain; the

†Sometimes macromolecules in which f branches are attached to a single "point" (Fig. 1*c*) are regarded as a separate class of starlike macromolecules.

variation of the g-factor with the number of branches p for trifunctional nodes is of the form [17]:

$$g_3(p) = \frac{1}{p^2}\left\{25 + 6(p+3)\left[\frac{\ln(p+3)}{\ln 2} - 3\right]\right\} , \quad (8)$$

and that for the tetrafunctional is:

$$g_4(p) = \frac{1}{p^2}\left\{10 + 3(p+2)\left[\frac{2\ln(p+2)}{\ln 3} - 3\right]\right\}. \quad (9)$$

Table 1. Numerical values of the g-factor.

f	b	Statistically branched polymers		Comblike branched polymers		f	b	Statistically branched polymers		Comblike branched polymers	
		g_1	g_2	g_1	g_2			g_1	g_2	g_1	g_2
3	1	0.900	0.778	0.900	0.778	4	1	0.800	0.625	0.800	0.625
	2	0.829	0.712	0.829	0.712		2	0.691	0.545	0.691	0.545
	3	0.774	0.668	0.774	0.668		3	0.618	0.496	0.618	0.496
	4	0.730	0.633	0.733	0.638		4	0.566	0.460	0.569	0.465
	5	0.694	0.605	0.703	0.617		5	0.525	0.432	0.534	0.443
	6	0.663	0.581	0.679	0.601		6	0.493	0.410	0.508	0.428
	7	0.636	0.560	0.660	0.589		7	6.466	0.391	0.488	0.416
	8	0.613	0.542	0.645	0.580		8	0.443	0.374	0.472	0.407
	9	0.592	0.525	0.632	0.572		9	0.423	0.360	0.459	0.400
	10	0.573	0.510	0.622	0.566		10	0.406	0.347	0.448	0.394
	12	0.541	0.485	0.605	0.556		12	0.378	0.326	0.431	0.385
	15	0.505	0.454	0.587	0.546		15	0.344	0.301	0.414	0.375
	20	0.454	0.414	0.567	0.535		20	0.305	0.270	0.395	0.365
	25	0.418	0.384	0.555	0.529		25	0.277	0.248	0.384	0.359
						8	1	0.53	0.35	—	—
							2	0.41	0.28	—	—
							3	0.34	0.24	—	—

Note: g_1 random distribution of branch lengths; g_2 fixed branch lengths.

The results given in Table 1 relate to an idealised example in which monodisperse linear and branched polymers are compared and all the branched molecules have the same number of branching nodes. In practice, however, there is always a definite scatter both in the molecular weight and in the number of branching nodes for different macromolecules. Leaving aside the problem of the breadth of the molecular weight distribution, we will point out that for homogeneous polymers the molecules of which have a different number of branching nodes, Zimm and Stockmayer [12] obtained an equation relating the averaged mean square dimensions of molecules of such a polymer to the mean number of branching nodes b_n per molecule. For trifunctional branching nodes the mean value of the g-factor equals‡:

$$\langle g_3(b)\rangle = \left(\sqrt{1 + \frac{b_n}{7}} + \frac{4b_n}{9\pi}\right)^{-1/2} \quad (10)$$

and that for the tetrafunctional nodes is:

$$\langle g_4(b)\rangle = \left(\sqrt{1 + \frac{b_n}{6}} + \frac{4b_n}{3\pi}\right)^{1/2} . \quad (11)$$

The values of $< g(b) >$ are characteristic for fractions of the branched polymer if the fractionation proceeds only according to the molecular weights. These values are given in Table 1.

‡The sign $<>$ denotes the mean of the quantity considered.

It is noteworthy that not only do long-chain branchings lead to an appreciable decrease in the dimensions of the macromolecules; it is known that for comblike molecules with a large number of short side-chain attachments of the same length, the value of the g-factor is given by [18]:

$$g = \frac{n - \sum_\lambda n_\lambda}{n} = \frac{n_x}{n} \quad (12)$$

where n is the total number of segments in the macromolecule, n_λ the number of segments in the λ side chain, and n_X the number of segments in the "spine" of the macromolecule. Ptitsyn [15] obtained a similar relation:

$$g = \frac{m}{m+n} \quad (12a)$$

(see Fig. 1).

By short side branches is understood those branches with a length comparable with the distance between them ($m \simeq n$). Hence when there is a large number of short side attachments ($n_\lambda/n \ll 1$) the value of the g-factor can also differ considerably from unity. However, unlike the long-chain branching in this instance the dimensions of the macromolecules are determined mainly by the length of the spine; it is then possible in principle for 99% of the mass of the macromolecule to be centred in the side-chains of the branches. Such macromolecules can have anomalously small dimensions for a large molecular weight. As Eqns. (12) and (12a) show, the value of the g-factor depends not only on the number but also on the lengths of the side-chains, therefore the determination of the number of nodes solely from the g-factor cannot be considered reliable for short-chain branching.

Direct measurements of the mean sizes of the macromolecules can be made using a light scattering method but this method is as yet little used in analysing branching. The theory of the scattering of light by branched macromolecules has been developed only for certain particular instances [19-21], therefore these problems will not be discussed here. The present investigation of branching is now mainly on the basis of a study of the hydrodynamic behaviour of macromolecules in solutions (characteristic viscosity and sedimentation).

IV. HYDRODYNAMIC PROPERTIES OF BRANCHED MACROMOLECULES

Branched polymers in which the branching density does not exceed the critical value dissolve in the same solvents as do the linear polymers. However, in several studies it was noted that the solubility of branched polymers is less than that of linear, since the critical temperature of mixing of a polymer with a solvent for branched polymers is higher than for linear polymers of equal molecular weight [22,23].

In thermodynamically ideal solvents linear macromolecules can be regarded as unflowing coils with a gaussian distribution of the segments around the centre of gravity. The appearance of branching leads to a concentration of the segments and their more uniform distribution in the volume of the macromolecule, therefore the statistics of a branched macromolecule in solution are gaussian [25,26]. In this sense the effect of branching is opposite to the influence of phenomena of the volume effects (well studied theoretically) [10,24] in "good" solvents, where the "dilution" of the segments in the bulk of the macromolecule is observed.

1. Sedimentation and Diffusion of Branched Macromolecules

The sedimentation constant S and diffusion constant D of the macromolecules are connected with their dimensions by the coefficient of translational friction F_{tr} (here and subsequently reference is made to the sedimentation and diffusion constants extrapolated to infinite dilution):

$$S = \frac{M(1-\bar{v}\rho_0)}{NF_{tr}} \quad (13)$$

$$D = \frac{kT}{F_{tr}} \quad (14)$$

$$F_{tr} = P(\overline{R^2})^{1/2}\eta_0 = B\eta_0 \quad (15)$$

where M is the molecular weight, $\bar{v}$ the specific partial volume of the polymer, η_0 and ρ_0 are the viscosity and density of the solvent, N is Avogadro's number, k the Boltzman constant, and P the Flory constant, which characterises the hydrodynamic interaction of the macromolecules with the solvent in translational motion for linear polymers in a θ-solvent, $P = 5.11 \times \sqrt{6}$. The sedimentation and diffusion constants are determined by the first power of the hydrodynamically effective dimensions of B. Application of Eqns. (13)–(15) to linear and branched macromolecules gives:

$$\frac{S_b}{S_l} = \frac{D_b}{D_l} = \frac{P_l(\overline{R_l^2})^{1/2}}{P_b(\overline{R_b^2})^{1/2}} = \frac{P_l}{P_b}g^{-1/2}; \quad (16)$$

$$\frac{P_l(\overline{R_l^2})^{1/2}}{P_b(\overline{R_b^2})^{1/2}} = \frac{B_l}{B_b} = h; \quad (17)$$

$$\frac{S_b}{S_l} = \frac{D_b}{D_l} = \frac{F_{tr,b}}{F_{tr,l}}, \quad (18)$$

where h is the ratio of the dimensions hydrodynamically effective in forward motion; the subscripts b and l refer to branched and linear macromolecules.

On the basis of the Kirkwood and Riseman theory of the hydrodynamic properties of macromolecules [28,29], Stockmayer and Fixman [27], Ptitsyn [15], and Kurata and Fukatsu [16] made direct calculations of the ratio of the coefficients of friction and of the sedimentation and diffusion constants of branched and linear macromolecules of the same molecular weight. For starlike molecules with a fixed branch length the following relation was found [27] between the ratio of the hydrodynamic dimensions h and the branching functionality f:

$$h = \frac{f^{1/2}}{2-f+\sqrt{2}(f-1)} \quad (19)$$

The values of h for comblike and statistically branched macromolecules were calculated by Ptitsyn [15] and by Kurata and Fukatsu [16]; the corresponding analytical expressions are extremely large and will not be given here; calculated values for the various types of branching are given in Table 2. It is noteworthy that concordant results were obtained in these studies [15,16].

Kurata and Fukatsu [16] showed that for statistically branched macromolecules the ratio P_b/P_l increases monotonically with increase in the branching density, tending to the asymptotic value of 1.34. As the branching density is increased, for graft branched macromolecules the value of the ratio P_b/P_l first rises then passes through a maximum and decreases, tending to 1.00 independent of the functionality of the branching. These results show that the hydrodynamically effective dimensions in translational motion of the macromolecules depend not only on the density but also the type of branching. In principle the relation $h = f(p)$ could be used for finding the branching type but in practice this is made difficult, since significant differences in the behaviour of the function $h = f(p)$ start only when the number of branching nodes reaches 30–40§.

Table 2. Numerical values of h.

f	b	Statistically branched polymers		Comblike branched polymers		f	b	Statistically branched polymers		Comblike branched polymers	
		h_1	h_2	h_1	h_2			h_1	h_2	h_1	h_2
3	1	0.972	0.947	0.972	0.947	4	1	0.938	0.892	0.938	0.892
	2	0.950	0.922	0.950	0.922		2	0.891	0.850	0.891	0.850
	3	0.931	0.903	0.931	0.903		3	0.864	0.820	0.864	0.820
	4	0.915	0.887	0.916	0.888		4	0.838	0.797	0.840	0.799
	5	0.901	0.873	0.903	0.876		5	0.817	0.778	0.820	0.782
	6	0.888	0.861	0.892	0.866		6	0.799	0.762	0.807	0.769
	7	0.878	0.850	0.883	0.858		7	0.782	0.748	0.791	0.757
	8	0.867	0.840	0.875	0.851		8	0.768	0.735	0.781	0.748
	9	0.855	0.831	0.868	0.845		9	0.755	0.724	0.771	0.740
	10	0.846	0.823	0.862	0.840		10	0.743	0.713	0.763	0.733
	12	0.830	0.807	0.852	0.830		12	0.723	0.695	0.749	0.721
	15	0.808	0.788	0.839	0.820		15	0.697	0.672	0.733	0.708
	20	0.779	0.760	0.825	0.807		20	0.664	0.642	0.714	0.692
	25	0.756	0.739	0.814	0.798		25	0.638	0.619	0.701	0.681
						8	1	0.81	0.72	—	—
							2	0.73	0.66	—	—
							3	0.68	0.62	—	—

Note: h_1 random distribution of branch lengths; h_2 fixed branch lengths.

2. Characteristic Viscosity of Branched Monodisperse Polymers

The characteristic viscosity, $[\eta]$, in a θ-solvent is connected with the unperturbed mean square dimensions of the test macromolecules by the following relation:

$$[\eta] = \Phi\frac{(\overline{R^2})^{3/2}}{M}; \quad (20)$$

where Φ is Flory's constant, characterising the hydrodynamic interaction of macromolecules with the solvent in rotational motion; for linear polymers in a θ-solvent $\Phi = 6^{3/2} \times 2.86 \times 10^{21}$. Evidently the characteristic viscosity depends not only on the dimensions of the macromolecules but also on the nature of their hydrodynamic interaction with the solvent. When allowance is made for this the characteristic viscosity is determined by the cube of the hydrodynamically effective dimensions A:

$$[\eta] = \frac{A^3}{M}. \quad (20a)$$

From Eqn. (20) the characteristic viscosity of the branched macromolecules should be less than that for linear polymers of the same molecular weight. The use of Eqns. (20) and (20a) for linear and branched polymers leads to the following relations:

$$\frac{[\eta]_b}{[\eta]_l} = \frac{\Phi_b}{\Phi_l}\left(\frac{\overline{R_b^2}}{\overline{R_l^2}}\right)^{3/2} = \frac{\Phi_b}{\Phi_l}\cdot g^{3/2}, \quad (21)$$

$$\frac{[\eta]_b}{[\eta]_l} = \frac{A_b^3}{A_l^3}. \quad (22)$$

§While this paper was in the press a paper by Berry [82] dealing with the calculation of the coefficient of translational friction of statistically branched macromolecules of comblike structure appeared.

The value of the ratio of the hydrodynamic interaction constants Φ_b/Φ_1 of branched and linear polymers is determined by the statistics of the macromolecular coil in the solution. Many calculations [15,16,27,30] have shown that the effect of branching on the geometric dimensions is more pronounced than on the hydrodynamic parameters, in other words, the hydrodynamic interaction of branched macromolecules with a solvent is stronger than that of linear, that is, $\Phi_b/\Phi_1 > 1$. Assuming that hydrodynamically effective dimensions in translational and rotational motion of macromolecules are the same, $A = B$, Stockmayer and Fixman [27] obtain for models of star-shaped branched molecules the following relation (in this instance the functionality agrees with the number of branches):

$$\frac{[\eta]_b}{[\eta]_1} = h^3 = \frac{f^{3/2}}{\{2 - f + \sqrt{2}\,(f-1)\}^{3/2}}. \qquad (23)$$

On the other hand, for the model under consideration

$$g = \frac{3f-2}{f^2}. \qquad (24)$$

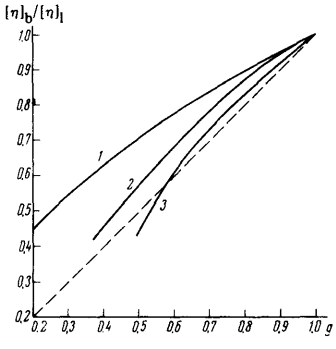


Figure 2. Variation of the characteristic viscosity with the g-factor: *1*) Zimm–Kilb theory; *2*) and *3*) calculated by Eqn. (25); *2*) Stockmayer and Fixman's results; *3*) Kurata and Fukatsu's results ($f = 3$, statistically branched); broken line, the relation $[\eta]_b/[\eta]_1 = g$.

On eliminating f from Eqns. (23) and (24), the variation of the ratio of the hydrodynamic dimensions, that is, the ratio of the characteristic viscosities (sedimentation constant) of branched and linear macromolecules with the g-factor can be found (Fig. 2, curve *1*). In practice, however, examples are seldom encountered in which the functionality of the branching exceeds 8. On also allowing for the fact that in this instance the presence of only one branching node is assumed it is evident that the use of Eqns. (23) and (24) is extremely limited in principle. Therefore Stockmayer and Fixman assume that the relation $h^3 = f(g)$ remains valid for any model of branching and propose to use it for finding not only the functionality but also the number of branching nodes if the relation $[\eta]_b/[\eta]_1$ is known.

Zimm and Kilb [30] attempted to find whether there is actually any general connection between the ratio of the characteristic viscosities of branched and linear macromolecules and the value of the g-factor beyond the dependence on the nature of the branching. On the basis of the Kirkwood–Riseman theory [28,29] of hydrodynamic properties of macromolecules, within the framework of the "pearl necklace" model, Zimm and Kilb directly calculated the value of the characteristic viscosity for two models of starlike branching of macromolecules: (1) one branching node with four branches of equal length; (2) one branching node with two long and eight short branches. The results of these calculations lead to the conclusion that for both branching models examined the following approximate relation is valid:

$$[\eta]_b/[\eta]_1 \cong g^{1/2}; \qquad (25)$$

Zimm and Kilb also suggest that this equation can be applied with good approximation to any type of branched macromolecules.

It is noteworthy that the Stockmayer–Fixman and the Zimm–Kilb calculations were carried out for starlike macromolecules and *a priori* extension of results to comb-like macromolecules give rise to objections. We think that the more accurate relation $[\eta]_b/[\eta]_1 = f(g)$ for comb-like and statistically branched polymers can be obtained on the basis of calculations of hydrodynamically effective dimensions of macromolecules made by Kurata and Fukatsu [16] (Table 2). Here again it is suggested that the relation

$$[\eta]_b/[\eta]_1 = h^3 \qquad (26)$$

is valid.

Fig. 2 gives the results of calculations of the relation $[\eta]_b/[\eta]_1 = f(g)$, which we made with allowance for Eqn. (26), according to Stockmayer and Fixman's and to Kurata and Fukatsu's results and according to Zimm and Kilb's theory. It should be noted that Eqn. (26) evidently over-rates the influence of branching on the value of the characteristic viscosity, especially in the range of high branching densities, where the hydrodynamic interaction increases considerably, therefore the true $[\eta]_b/[\eta]_1 = f(g)$ curves for models considered by Stockmayer and Fixman, and by Kurata and Fukatsu rule out some of the above references.

The existence of the relation $h = f(g)$ allows the degree of branching of a polymer with a narrow MWD to be evaluated on the basis of measurements of the characteristic viscosity or sedimentation (diffusion). Knowing the ratio of the hydrodynamic dimensions (that is, the ratio of the characteristic viscosities or sedimentation constants) of branched and linear macromolecules of equal molecular weight and of equal branching type, the corresponding ratio of geometric dimensions (the g-factor) and then from tables the number of nodes (branches) in a macromolecule can be found.

V. DEGREE OF BRANCHING IN POLYDISPERSE POLYMERS

Most of the synthetic polymers which are dealt with in practice are polydisperse. The degree of branching of polydisperse polymers is estimated by averaging the corresponding characteristics of monodisperse branched polymers. The concept of mean density of branching is introduced as a quantitative characteristic of branched polydisperse polymers. The number average branching density b_n is determined by the expression:

$$b_n = \frac{\sum_{x=1}^{\infty}\sum_{b=0}^{\infty} bP_{b,x}}{\sum_{x=1}^{\infty}\sum_{b=0}^{\infty} P_{b,x}}, \qquad (27)$$

where $P_{b,x}$ is the number of molecules of degree of polymerisation x, having b branching nodes, and b_n the mean number of branching nodes for a single polymeric molecule. The weight average branching density b_w is determined similarly:

$$b_w = \frac{\sum_{x=1}^{\infty}\sum_{b=0}^{\infty} b_x P_{b,x}}{\sum_{x=1}^{\infty}\sum_{b=0}^{\infty} x P_{b,x}}. \quad (28)$$

Before analysing the value of the characteristic viscosity of polydisperse branched polymers we will examine the principal functions of MWD of branched polymers.

1. MWD of Branched Polymers

Branched polymers are usually characterised by wider molecular weight distribution functions than for linear ones, a polydispersity index determined as the ratio of the mean weight index of polymerisation x_w to the numerical mean x_n for branched polymers is usually greater than two, $x_w/x_n > 2$. Here we will consider some MWD functions typical for branched polymers.

The MWD of a polymer formed in the common statistical polycondensation of bi- and tetra-functional monomeric units is described by the distribution function given by Stockmayer [31], which can be represented as a system of equations:

$$P_{0,x} = x/y_n^2 \exp\{(x/y_n)(1+\gamma/2)\},$$
$$P_{b,x} = \frac{\gamma (x/y_n)^2}{2b(2b+1)(2b+2)} P_{b-1,x}, \quad (29)$$

where γ is the branching index—see Eqn. (3), y_n the number average degree of polymerisation of the corresponding linear polymer, which would be obtained were the tetrafunctional units replaced by the stoichiometric amount of bifunctional units, and a polymer with "most probable" MWD is formed. The mean degrees of polymerisation of the branched x and linear y polymers thus obtained are connected by the relations [31]:

$$x_w = \frac{y_w}{1-\gamma}; \quad (30)$$
$$x_n = \frac{y_n}{1-\gamma/4}; \quad (31)$$
$$y_w = 2y_n. \quad (32)$$

The branching parameter γ is connected with the number average b_n and the weight average b_w by the number of branching nodes by the following equations:

$$b_w = \frac{\gamma}{1-\gamma}; \quad (33)$$
$$b_n = \frac{\gamma}{4-\gamma}. \quad (34)$$

A variant of the Stockmayer function for polymers with trifunctional branching nodes (common polycondensation of bi- and tri-functional units) was obtained by Schultz [32]:

$$P_{0,x} = x/y_n^2 \exp\{-x/y_n(\gamma+1)\}; \quad P_{b,x} = \frac{\gamma (x/y_n)^2}{b(b+2)} P_{b-1,x}. \quad (35)$$

Fig. 3*a* shows a Stockmayer-type MWD for polymers with trifunctional and tetrafunctional branching nodes and various γ, the "most probable" distribution being given. Clearly the increase in the degree of branching leads to the appearance of high-molecular-weight "tails" and the MWD maximum is shifted to lower molecular weights; such regularities are actually observed in the synthesis of branched polystyrenes [33] and polybutadienes [34]. For a MWD describable by the system of equations (35), the following relations are obeyed:

$$x_w = \frac{y_w}{1-\gamma}; \quad (36)$$
$$x_n = \frac{y_n}{1-\gamma/3}; \quad (37)$$
$$b_w = \frac{2\gamma}{1-\gamma}; \quad (38)$$
$$b_n = \frac{{}^2/_3\gamma}{1-\gamma/3}. \quad (39)$$

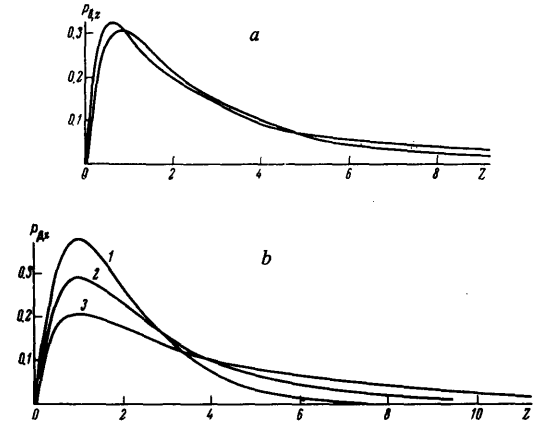


Figure 3. MWD of branched polymers, $Z = x/y_n$: *a*) MWD of the Stockmayer type, $f = 3:1$; *1*) $\gamma = 0.96$; *2*) $\gamma = 0.40$; *b*) MWD of the Beasley type, β: *1*) 0; *2*) 0.2; *3*) 0.499.

Another important distribution function was given by Beasley [35] for the MWD of polymers in the preparation of which the termination of the growing chains is brought about by disproportionation, conversion to the monomer, and conversion to a polymer (trifunctional branching), analytically the Beasley function is expressed by Eqn. (40) (Fig. 3*b*):

$$P_{\beta,x} = \frac{x/y_n^2}{(1+\beta x/y_n)^{1+1/\beta}} \quad (\beta < {}^1/_2), \quad (40)$$

where β is a long-chain branching parameter, equal to the ratio of the number of units in the side-branches and their total number in the macromolecule, with [35,36]:

$$x_n = \frac{y_n}{1-\beta}; \quad (41)$$
$$x_w = \frac{y_w}{1-2\beta}; \quad (42)$$
$$b_n = \frac{\beta}{1-\beta}; \quad (43)$$
$$b_w = \frac{1}{(1-\beta)(1-2\beta)} - 1. \quad (44)$$

Under comparable conditions the Beasley distribution is wider than the Stockmayer distribution. From Eqns. (30)–(34), (36)–(39), and (41)–(44) we obtain the frequently

used relations connecting the polydispersion of the polymer with the mean number of branching nodes:

$$\left.\begin{aligned}\frac{x_w}{x_n}&=\frac{2}{3}\frac{b_w}{b_n};\\ \frac{x_w}{x_n}&=\frac{2}{1-b_n};\end{aligned}\right\}\quad\begin{aligned}&\text{Stockmayer distribution}\\&\text{trifunctional nodes}\end{aligned}\qquad(45),\ (46)$$

$$\left.\begin{aligned}\frac{x_w}{x_n}&=\frac{1}{2}\frac{b_w}{b_n};\\ \frac{x_w}{x_n}&=\frac{2}{1-3b_n};\end{aligned}\right\}\quad\begin{aligned}&\text{Stockmayer distribution}\\&\text{(tetrafunctional nodes)}\end{aligned}\qquad(47),\ (47a)$$

$$\left.\begin{aligned}\frac{x_w}{x_n}&=\frac{1}{2}\left(\frac{b_w}{b_n}-1\right);\\ \frac{x_w}{x_n}&=\frac{2}{1-b_n}\end{aligned}\right\}\quad\text{Beasley distribution}\qquad(48),\ (48a)$$

Certain parameters of the branched polydisperse polymers with the Beasley-type and Stockmayer-type MWD are also shown in Table 3. Other MWD functions for branched polymers obtained in various polymerisation processes and also for the cross-linking and destruction were given detailed consideration by Bamford and Tompa [37], Katsura [38], Spiro [39], etc.

2. Characteristic Viscosity of Branched Polymers

We will assume that for monodisperse polymers the following relations are true:

$$[\eta]_b = g^{1/2}[\eta]_l, \qquad (49)$$

$$[\eta]_l = K_\eta x^a, \qquad (50)$$

where x is the degree of polymerisation, K_η and a are constants for the given series of polymer homologues.

Furthermore let $f(x)$ and $f(\gamma, x)$ be the weight functions of the distribution according to the degree of polymerisation for a linear and a diluted polymers, and γ a branching parameter determinable so that

$$f(\gamma, x)|_{\gamma\to 0} = f(x). \qquad (51)$$

On averaging in accordance with Eqns. (49) and (50) we obtain the following equation for the ratio of the characteristic viscosities of the branched and linear polydisperse polymers:

$$\langle[\eta]_b\rangle/\langle[\eta]_e\rangle = \frac{\int_0^\infty K_\eta g_x^{1/2} x^a f(x,\gamma)\,dx}{\int_0^\infty K_\eta x^a f(x)\,dx}. \qquad (52)$$

By using Eqns. (30) and (36) and taking into account that linear and branched polymers with the same mean weight are being compared, Eqn. (52) can be converted into [40]:

$$\langle[\eta]_b\rangle/[\eta]_e\rangle = (1-\gamma)^a \frac{\int_0^\infty g_x^{1/2} x^a f(\gamma, x)\,dx}{\int_0^\infty x^a f(x)\,dx}. \qquad (53)$$

The calculation of $<[\eta]_b>/<[\eta]_l>$ with the aid of Eqn. (53) is carried out as follows:

1. By using the MWD functions (29), (35), and (40), the number average values of the branching nodes b_n for various x are determined.

2. From the values for b_n, the corresponding values of $g_x^{1/2}$ are found on the basis of Stockmayer's equations (10) and (11).

3. By using the values found for x, $g_x^{1/2}$, and $f(\gamma, x)$ and replacing integration by summation the value of the numerator in Eqn. (53) is calculated.

4. The value of the denominator is expressed by elementary functions. A complete calculation of the ratio $<[\eta]_b>/<[\eta]_l>$ for polydisperse polymers with a Stockmayer-type MWD (with γ variable) was made on an electronic computer by Klib [40] for the tetrafunctional nodes and by Shultz [32] for trifunctional branching nodes (Table 3) and by Myers and Dagon [41] for a Beasley-type MWD.

Table 3. Ratio of the characteristic viscosities of branched and linear polymers of the same mean molecular weight (MWD of the Stockmayer type).

γ	$[\eta]_b/[\eta]_l$				
	$f=3$			$f=4$	
	$a=0.50$	$a=0.66$	$a=1.00$	$a=0.50$	$a=0.68$
0.1	0.975	0.974	0.978	—	—
0.2	0.948	0.946	0.954	0.94	0.94
0.3	0.917	0.914	0.926	—	—
0.4	0.880	0.875	0.892	0.87	0.87
0.5	0.839	0.832	0.855	—	—
0.6	0.787	0.778	0.807	0.77	0.76
0.7	0.722	0.709	0.744	—	—
0.8	0.633	0.614	0.654	0.61	0.58
0.9	0.490	0.462	0.501	0.47	0.43
0.92	0.450	0.421	0.463	—	—
0.94	0.402	0.371	0.415	—	—
0.96	0.342	0.308	0.364	—	—

The results of Table 3 can be used in evaluating the branching of polydisperse polymers on the basis of measurements of characteristic viscosity. For this a knowledge of the characteristic viscosity of the linear polymer with the "most probable" distribution and the same weight mean molecular weight is necessary. If the value of x_w is known the corresponding value of $<[\eta]_l>$ can be determined by using the equation for the dependence of characteristic viscosity on molecular weight for linear monodisperse polymers

$$[\eta]_l = K_\eta x^a, \qquad (50a)$$

which are usually found in investigating hydrodynamic characteristics; the corresponding equation for the weight mean degree of polymerisation in a θ-solvent has the form [42]:

$$\langle[\eta]_l\rangle = \frac{K_\eta}{1.14} x_w^a. \qquad (54)$$

In principle the ratio $<[\eta]_b>/<[\eta]_l>$ can be compared at the same values of number mean molecular weight, but this method appears less sensitive to branching than that described above [40].

It is noteworthy that estimation of branching of polydisperse polymers with the aid of the $<[\eta]_b>/<[\eta]_l>$ dependence, strictly speaking, is valid only in those instances when the branching reaction leads to the departure of the MWD of polymers from the most probable.

The influence of the form of the MWD functions on the value of $<[\eta]_b>/<[\eta]_l>$ is clear from Table 4, which gives values calculated on the basis of Beasley-type [41] and Stockmayer-type [32] MWD (trifunctional nodes) at equal values

of x_w/x_n (the MWD of a linear specimen is considered "most probable"), with

$$\gamma = \frac{3\beta}{2-\beta}. \quad (55)$$

At equal values of x_w/x_n the Beasley distribution is wider than the Stockmayer distribution; as Table 4 shows, this leads to some decrease (by 6–14%) in the values of $\langle[\eta]_b\rangle/\langle[\eta]_l\rangle$. The Beasley distribution is known to somewhat overestimate the breadth of the experimentally observable curves[41,42] of branched polymers, therefore the use of results obtained with the aid of the Stockmayer equation is evidently more correct.

Table 4. Ratio of the characteristic viscosities of branched and linear polymers depending on the MWD of the branched polymer ($f = 3$).

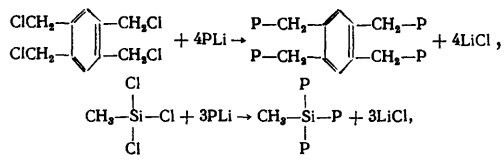
β	x_w/x_n	γ	$\langle[\eta]_b\rangle/\langle[\eta]_l\rangle$	
			Beasley distribution	Stockmayer distribution
0.05	2.11	0.077	0.922	0.981
0.10	2.25	0.158	0.901	0.960
0.15	2.43	0.243	0.876	0.935
0.20	2.67	0.333	0.847	0.906
0.25	3.00	0.429	0.809	0.869
0.30	3.50	0.529	0.763	0.826
0.35	4.33	0.636	0.700	0.766
0.40	6.00	0.750	0.612	0.680
0.45	11.0	0.871	0.465	0.542

In concluding this section it must be emphasised that all the calculated values of $\langle[\eta]_b\rangle/\langle[\eta]_l\rangle$ obtained under the condition that Eqn. (49) is valid are derived, strictly speaking, for the polymer solvent θ-system ($\alpha = 0.5$), therefore the problem of measurements in "good" solvents for the purpose of evaluating the branching still remains open, and corresponding experimental results will be considered below.

VI. SYNTHESIS AND INVESTIGATION OF MODEL BRANCHED POLYMERS

In most polymerisation processes it was previously impossible to predict the number of nodes associated with a single polymeric molecule, the lengths of the branches, the nature of their distribution, or even the functionality of the branching. Therefore it is very difficult to make a strict comparison between the values calculated theoretically under definite conditions and the same quantities observable experimentally. With the aim of surmounting this difficulty attempts were made to synthesise model branched polymers with a geometry known beforehand.

Starlike macromolecules can serve as the simplest models. This type of model polymer is synthesised with the aid of "living" polymeric chains and bonding agents such as 1,2,4,5-tetrachlorobenzene, silicon tetrachloride, methyltrichlorosilane, etc. Several papers[44–48] describe methods of production and give structural characteristics for tri- and tetra-functional starlike polymers of styrene and butadiene; the synthesis proceeds as follows:



where PLi denotes a "live" polymeric chain.

Ideally all the chlorine atoms are replaced by a polymer anion; hence if the initial polymer molecules have a narrow MWD, as a result almost monodisperse branched polymers with a tripled or quadrupled molecular weight are formed. In practice, as a result of incomplete replacement and of side-reactions a mixture of molecules of different molecular weight and functionality is obtained, however, the choice of appropriate conditions gives an overwhelming yield of molecules of the specified structure.

Table 5. Characteristic of branched polystyrenes[45,46,48].

No.	$10^{-3}M_w$	p	M_w/M_n	$[\eta]$ good solvent	$[\eta]_\theta$	$[\eta]_b/[\eta]_l$ good solvent	$[\eta]_b/[\eta]_l$ θ-solvent	$[\eta]_b/[\eta]_l$ theory
				$f=3$	$b=1$			
1	170	3.0	—	0.563	0.288	0.90	0.94	
2	258	2.8	—	—	0.360	—	0.84	0.88*
3	348	2.6 3.1	0.99	0.976	0.435	0.88	0.85	0.85**
				$f=4$,	$b=1$			
1	11	3.9	—	—	0.077	—	0.86	
2	215	3.7	—	—	0.309	—	0.79	
3	363	3.9 3.9	—	—	0.390	—	0.75	0.79*
4	257	4.9 4.1	—	0.705	0.309	0.84	0.82	0.71**

*Zimm–Kilb theory.
**Stockmayer–Fixman theory.

Furthermore, to obtain polymers with high homogeneity both in respect of molecular weights and of the functionality of branching further fractionation is employed, which in this instance is especially effective owing to the great difference in the molecular weights. Sufficiently homogeneous, but low-molecular-weight, branched polymers are evidently formed in the synthesis of polyamides of star structure[49], and also of polyhedra from monodisperse blocks of polyethylene glycols with the aid of the trichloride of trimesic acid and other compounds[50]. Some experimental results for model branched (starlike structure) polymers of styrene are given in Table 5, where p is the value found experimentally for the mean number of branches attached to one molecule.

A method of controlled synthesis making use of the chain transfer reaction to a polymer (with narrow MWD) introduced earlier into the reaction zone has been used[51] for obtaining comblike trifunctional poly(vinyl acetates) with a fixed side-chain length, and with random distribution of the branches along the main "spine". Homogeneous branched polymers with short side-chains of known number and length were thus obtained; statistically branched poly(vinyl acetates) have been synthesised[52]. Fig. 4 and Table 6 give some results from published studies[52,53].

From Tables 5 and 6 and Fig. 4 and also from other experimental results[30,49,50], the appearance of branching actually leads to a decrease in the characteristic viscosity of the corresponding polymers in comparison with the linear ones of equal molecular weight, and the viscosity of the statistically branched polymers is less than that of the comblike ones. The variation predicted theoretically for a θ-solvent of the ratio of the characteristic viscosities of branched and linear polymers at a fixed molecular weight[30], see Eqn. (25), is obeyed satisfactorily for star-like polymers of various chemical structures.

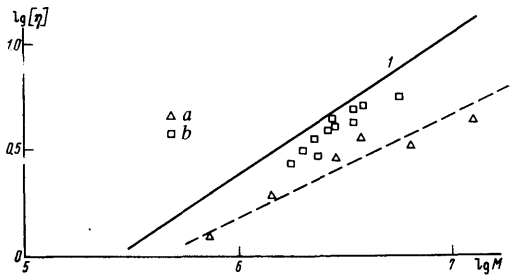


Figure 4. Variation of the characteristic viscosity of poly(vinyl acetates) in benzene at 35°C: *1*) linear structure, $[\eta] \simeq M^{0}$;[68] *a*) statistical branching, $[\eta] \simeq M^{0.47}$; *b*) comblike branching.

It is noticeable, however, that most of the model polymers contained only one branching node, therefore it is evidently still early to extend rule (25) to the region of high branching densities. Furthermore in some instances, for example, for polyethylenes[43] of the high pressure type, poly(vinyl acetates)[53], and other polymers, appreciable departures from the rule are observed, namely, the number of nodes calculated with the aid of Eqn. (25) is greater than expected and for these polymers the relation

$$[\eta]_b/[\eta]_l = g^{\epsilon}, \qquad (56)$$

where $\epsilon > \frac{1}{2}$, holds, that is, Eqn. (25) underestimates the effect of branching.

From Table 6 it is evident that the value of $g^{1/2}$ systematically exceeds the ratio $[\eta]_b/[\eta]_l$ even in a good solvent; from this it follows that when there are a large number of short-chain branches Eqn. (25) also underestimates the effect of branching on the hydrodynamic properties.

Such anomalies are not remarkable, they must be expected at high branching densities, owing to the change in Φ_p (by analogy with P_p). Results on the model branched polymers with a considerable number of branching nodes are still extremely few and relate to polymers with short side-chains[51,53,54].

From the example of poly(vinyl acetate) (Table 6) clearly the ratio $[\eta]_b/[\eta]_l$ in a good solvent is usually greater than that in a θ-solvent and the value of the g-factor characterising the ratio of the dimensions in a θ-solvent is less than the directly measured ratio of the dimensions. This regularity agrees with a stated[55,56] viewpoint that volume effects should be stronger for branched polymers than for linear ones, therefore the characteristic viscosity of branched polymers should increase with improvement in the quality of the solvent more rapidly than the viscosity of the linear ones. However, on assuming that the Flory swelling coefficients α of linear and branched macromolecules are connected by the relation[53]:

$$\frac{\alpha_b^5 - \alpha_b^3}{\alpha_l^5 - \alpha_l^3} = \frac{C_b}{C_l} g^{-1/2}, \qquad (57)$$

where C_b and C_l are constants, which depend on statistics of branched and linear macromolecular coils in the solution, then the difference in the values of the ratios $([\eta_b]/[\eta]_l)_0$ and $([\eta]_b/[\eta]_l)$, should become appreciable only when the molecular weight becomes sufficiently high ($\sim$ 500 000). This can explain the fact that this regularity, observable for very high-molecular-weight polymers of vinyl acetate, was not observed for different model structures (Table 5) and the statistically branched polymers of lesser molecular weight[22,36,57,58].

Table 6. Characteristics of branched poly(vinyl acetates)[51-53].

No.	$10^{-6}M_w$	Molec. wt. of 1 branch	b	Wt. fraction of polymer in branches	g	$g^{1/2}$	$[\eta]_b/[\eta]_l$ good solvent	$[\eta]_b/[\eta]_l$ θ-solvent	R_b^2/R_l^2 good solvent
	12.6	—	—	—	0.32	0.57	0.35	—	0.58
	6.43	—	—	—	0.36	0.60	0.40	—	0.65
3	3.76	—	—	—	0.54	0.74	0.62	—	0.68
4	2.80	—	—	—	0.50	0.71	0.59	—	0.68
5	1.43	—	—	—	0.55	0.74	0.63	—	0.87
6	0.73	—	—	—	0.62	0.79	0.71	—	0.89
7	3.81	59	26	0.38	0.62	0.79	0.84	—	—
8	2.80	59	9	0.18	0.82	0.91	0.82	—	0.97
9	2.33	40	26	0.44	0.56	0.75	0.66	—	—
10	1.68	40	10	0.24	0.77	0.88	0.77	—	—
11	2.00	18.5	27	0.25	0.75	0.87	0.79	—	0.95
12	2.24	18	41	0.33	0.67	0.82	0.91	—	0.99
13	2.09	18	33	0.29	0.72	0.85	0.80	—	0.89
14	2.71	24	29	0.26	0.74	0.89	0.90	—	1.01
15	3.67	24.4	67	0.48	0.52	0.73	0.74	—	0.90
16	3.21	24.4	45	0.36	0.64	0.80	0.74	—	0.82
17	5.60	106	17	0.33	0.67	0.84	0.70	0.51	0.92
18	2.65	74.8	7	0.20	0.78	0.90	0.80	0.75	0.97
19	3.43	67	19	0.37	0.63	0.79	0.74	0.73	0.85
20	3.29	61	17	0.31	0.69	0.84	0.75	0.50	0.90
21	4.11	63.5	29	0.45	0.55	0.76	0.67	—	0.83
22	3.45	47	19	0.26	0.74	0.86	0.85	—	0.90
23	3.96	43.7	33	0.37	0.64	0.80	0.67	—	0.90

The synthesis of model branched polydisperse polymers with the aim of verifying the corresponding theoretical relations is a much more complex task. Nevertheless, attempts were made to synthesise polymers of vinyl acetate with a known degree of branching (that is, with b_n and b_w) and known MWD, using the method of controllable polymerisation with transfer of chains to the polymer. It has been found[36] that the value of the ratio $\langle[\eta]_b\rangle/\langle[\eta]_l\rangle$ is almost independent of the quality of the solvent, as for monodisperse polymers. Furthermore it has been shown that for the vinyl acetate polymers investigated the relation between the value of $\langle[\eta]_b\rangle/\langle[\eta]_l\rangle$ and the weight mean number of branches b_w there is just the same correlation as between $\langle g^{1/2}\rangle$ and b_w for polymers with a Stockmayer distribution[31]:

$$\langle g^{1/2}\rangle = \left(\frac{6}{b_w}\right)^{1/2}\left\{\frac{1}{2}\frac{2+b_w^{1/2}}{b_w}\ln\frac{(2+b_w)^{1/2}+b_w^{1/2}}{(2+b_w)^{1/2}-b_w^{1/2}} - 1\right\}^{1/2}. \qquad (58)$$

From this there must be a relation of type (25) in this instance:

$$\frac{\langle[\eta]_b\rangle}{\langle[\eta]_l\rangle} = \langle g^{1/2}\rangle. \quad (25a)$$

However, it was shown that this agreement can be accidental and can vary with the nature of the reactions which lead to the branching of the polymeric chains.

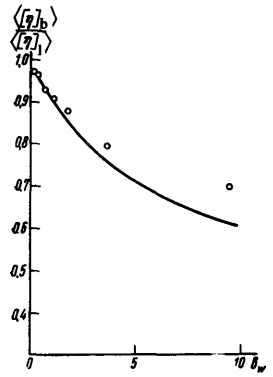


Figure 5. Variation of $[\eta]_b/[\eta]_l$ with the branching density for polymers with a Stockmayer-type MWD, with experimental points plotted from published results [36].

The decrease in the ratio $\langle[\eta]_b\rangle/\langle[\eta]_l\rangle$, expressed directly as a function of the number of branching nodes b_w, does not agree quite so well with the corresponding calculated relation obtained for trifunctional branched polymers with a Stockmayer-type MWD—calculated from the results of Table 4 and Eqn. (38), —see Fig. 5.

VII. VARIATION OF THE HYDRODYNAMIC PARAMETERS OF BRANCHED POLYMERS WITH MOLECULAR WEIGHT

The relations

$$[\eta]_l = K_{\eta l} M^{0.5}, \quad (59)$$

$$S_l = K_{Sl} M^{0.5}, \quad (60)$$

where $K_{\eta l}$ and K_{Sl} are coefficients which remain constant for a given series of polymer homologues, hold for linear monodisperse polymers in a solvent. In good solvents the value of the exponent in Eqns. (59) and (60) differs from 0.5. Most experimental studies on the investigation of branching have been carried out in good solvents and the dependence of the characteristic viscosity of branched polymers on molecular weight in logarithmic coordinates is usually bent towards the abscissa axis [22,33,59-62]. The explanation for this is that with increase in the molecular weight there is usually an increase in the branching density, therefore the dependence of the characteristic viscosity on molecular weight will be weakened, and the corresponding dependence of the sedimentation constant will be intensified; Eqns. (59) and (60) will become:

$$[\eta]_b = K_{\eta b} M^{0.5-\delta}, \quad (61)$$

$$S_b = K_{Sb} M^{0.5+\varphi}. \quad (62)$$

We will first examine the change in characteristic viscosity; from (59) and (61) we obtain:

$$[\eta]_b/[\eta]_l = K_1 M^{-\delta}. \quad (63)$$

In practice the greatest interest is in statistical and comblike branched macromolecules; it will be assumed that the increase in their molecular weight takes place by successive addition of branches of equal length with retention of the functionality of the branching. On assuming the correctness of the relation:

$$\langle[\eta]_b\rangle/\langle[\eta]_l\rangle = h^3,$$

we have:

$$h^3 = K' M^{-\delta}. \quad (64)$$

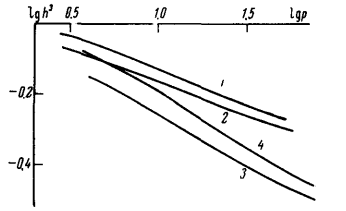


Figure 6. Variation of the ratio of the hydrodynamic dimensions of comblike branched and linear macromolecules with the number of branches: *1*) random distribution of branches with lengths $f = 3$; *2*) branches of equal length, $f = 3$; *3*) branches of equal length, $f = 4$; *4*) random distribution of branch lengths, $f = 4$.

Fig. 6 shows the relation:

$$\lg h^3 = f(\lg M)$$

for comblike branched macromolecules, $f = 3$ or 4, at a fixed branch length, calculated from Kurata and Fukatsu's results, where the number of branches is taken as a measure of the molecular weight; Fig. 6 also gives curves for the random distribution of the branches in length. Treatment of the results in Fig. 6 leads to the following results:

$f = 3$ { $\delta = 0.19$ branches of fixed length; $\delta = 0.20$ random distribution of branch lengths;

$f = 4$ { $\delta = 0.29$ branches of fixed length; $\delta = 0.31$ random distribution of branch lengths.

The values of δ are approximate (they were calculated by neglecting the low curvature of the curves discussed) and correct when the branching nodes lie between 3 and 20.

Earlier [58] for polymers with 1–4 trifunctional branching nodes and fixed branch lengths the value $\delta = 0.09$ was obtained by the relation

$$[\eta]_b/[\eta]_l = g^{1/2}$$

and $\delta = 0.12$ by calculation from Kurata and Fukatsu's results for the initial form of $h^3 = f(g)$ (1–4 nodes). Experimental results for dextranes [64] poly(vinyl acetates) [53], and polysiloxanes [65,66] with a large number of trifunctional

branching nodes, and for polybutadienes with a small number of nodes [47,63] agree satisfactorily with these calculations; for poly(vinyl acetates) $\delta = 20$, for polybutadienes $\delta = 0.09$, and for polysiloxanes $\delta = 0.22$ and 0.30.

Examples where the increase in molecular weight occurs only as a result of an increase in the functionality of the branches (a tenfold change in molecular weight produces a change in functionality from 3 to 30) will not be considered here because of their low practical importance. The value of δ differs from zero only if the increase in molecular weight is accompanied by an increase in the number of branching nodes because of their functionality; when the increase in molecular weight is due solely to the lengthening of the branches at $f = \text{const}$, $p = \text{const}$, then $\delta = 0$. Since

$$S_b / S_l = h^{-1},$$

it is evident that $\varphi = \delta/3$. Hence whereas the absolute value of the ratio of characteristic viscosities or sedimentation constants of the branched and linear macromolecules determine the length of the side-chains their dependence on molecular weight (especially in the range $b > 3$) can serve as an indicator of the functionality.

VIII. TREATMENT OF THE EXPERIMENTAL DATA IN STUDYING BRANCHING

As what has been said above shows, for a definite degree of branching of any polymer its hydrodynamic parameters must be compared with the parameters of the corresponding linear polymer of equal molecular weight, in other words, it is necessary to know the constants in the relation

$$[\eta]_l = K_l M^a \qquad (65)$$

for the linear polymer. However, this relation is not always known previously, and sometimes even the synthesis of the linear polymers presents difficulties. There are two main methods of studying branching in those instances when relation (65) is unknown. In both instances preliminary separation of the test polymer into a series of homogeneous fractions is necessary. The first method, based on the determination of the molecular weights of the fractions and working in a θ-solvent, was first used in studying branching in polymers of butadiene and isoprene [22,59,63].

Extension of the Flory theory of polymer solutions to branched molecules leads to the following relation [59]:

$$[\eta]^{3/2}/M^{1/2} = K_l^{3/2} g_{[\eta]} + 2C_M \psi K_l \frac{M}{[\eta]} g_{[\eta]}^{3/2}\left(1 - \frac{\theta}{t}\right); \qquad (66)$$

where ψ and C_M are constants for a given polymer–solvent system and

$$g_{[\eta]} = ([\eta]_b / [\eta]_l)^{3/2}.$$

From this equation, clearly whereas for linear polymers the relation at the temperature $T = \theta$ (in a θ-solvent) is expressed by a straight line parallel to the abscissa axis, for branched macromolecules this relation should have the form of a curve with negative slope, since $g_{[\eta]}$ in a disordered distribution of branching nodes decreases with rise in molecular weight. However, since as $M \to 0$ the number of branching nodes in the macromolecule also tends to zero and consequently $g \to 0$, the limiting value of $[\eta]^{2/3}/M^{1/3}$ remains as before equal to $K_l^{2/3}$. Hence by constructing this relation for branched polymers it is possible to determine the value of K_l and then by using the ratio $[\eta]_b/[\eta]_l$ to find the number of branches in the macromolecules of any molecular weight. Typical examples of the relation

$$[\eta]^{3/2}/M^{1/2} = f(M/[\eta])$$

for K-polybutadiene polymers obtained at various temperatures [22] are given in Fig. 7.

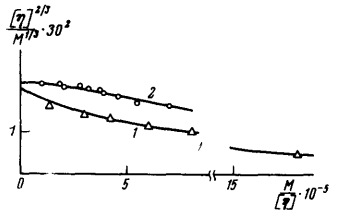


Figure 7. Variation of $[\eta]^{2/3}/M^{1/3}$ with $M/[\eta]$ in a solvent for polybutadienes of various structures: *1*) strongly branched; *2*) weakly branched.

Branching affects the hydrodynamic properties and dimensions, therefore there is a possibility in principle of obtaining information about the branching of macromolecules by direct measurement of any pair of hydrodynamic parameters connected with the coefficients of translational (diffusion, sedimentation) and rotational (characteristic viscosity) friction. This was first discussed by Tsvetkov [67].

This method of evaluating branching, based on combined measurements of sedimentation and characteristic viscosity, was proposed by Blachford and Robertson [68]; it is not necessary to know the molecular weight. It is known that

$$[\eta]_l = K_l M^a; \qquad (67)$$

$$S_l = K_s M^{\frac{1-a}{3}}. \qquad (68)$$

From Eqns. (67) and (68) we obtain

$$S_l = A[\eta]_l^{\gamma}; \qquad (69)$$

where A is a constant and

$$\gamma = \frac{2-a}{3a}. \qquad (70)$$

Applying the Flory theory to linear and branched polymers and assuming that

$$\Phi_l^{1/2} P_l^{-1} \cong \Phi_b^{1/2} P_b^{-1}, \qquad (71)$$

Blachford and Robertson [68] obtain

$$S_l [\eta]_l^{1/3} = S_b [\eta]_b^{1/3}. \qquad (72)$$

On substituting Eqn. (69) in (72) we have

$$A[\eta]_l^{\frac{3\gamma+1}{3}} = S_b [\eta]_b^{1/3}. \qquad (73)$$

Eqn. (73) is the principal one in this method; if γ, A, S_b, and $[\eta]_b$ are known, then the quantity $[\eta]_l$ can be obtained from Eqn. (73) and then the number of nodes in the macromolecules can be found in the usual way through the g-factor. A and γ are determined from the graph of $\lg S$ against $\lg[\eta]$ for fractions of the polymer being investigated, part of which is usually linear. An example of

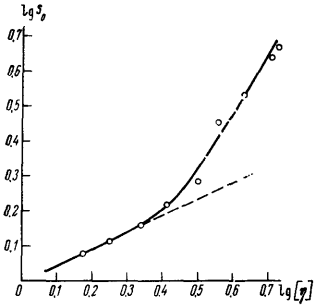


Figure 8. Variation of the sedimentation constants with the characteristic viscosity in benzene for fractions of butadienestyrene copolymer. The broken line corresponds with polymers of linear structure.

such a relation for fractions of emulsion butadienestyrene rubber are given in Fig. 8, and from the initial slope of the graph $A = 0.944$ and $\gamma = 0.61$. This method was used also for studying branching in polyurethanes [69]. The use of θ-solvents increases the accuracy of the method and its resolving power.

IX. OTHER METHODS OF DETERMINING DEGREE OF BRANCHING

The second virial coefficient A_2 is a measure of the interaction of polymer segments with one another in dilute solutions. The value of A_2 depends on the form of the intersegmental interaction potential and the statistics of the macromolecular coil in solution, approximate calculations of A_2 for certain models of starlike branched macromolecules have been given [70,71]. However, at present there is no complete and rigorous theory connecting the value of the second virial coefficient with the structure of branched macromolecules. The virial coefficient can be determined from osmometric and light scattering measurements¶:

$$\pi/c = \frac{RT}{M_n}(1 + A_2c + \ldots), \tag{74}$$

$$Kc/R_0 = \frac{1}{M_w}(1 + 2A_2c + \ldots), \tag{75}$$

where π is the osmotic pressure, R_0 the relative intensity of scattered light, c the concentration, and K a constant.

Extension of the theory of solutions of linear polymers to branched ones leads to the following approximate equation [44]:

$$(A_2)_b/(A_2)_l \cong g^{1/2}\left(\frac{\alpha_b}{\alpha_l}\right)^3, \tag{76}$$

where α_b and α_l are the swelling coefficients of linear and branched macromolecules respectively. Eqn. (76) is further simplified in the limiting case of large volume effects (high-molecular-weight polymer in a good solvent) [53]:

$$(A_2)_b/(A_2)_l = g^{1/2}. \tag{77}$$

¶Calculations of the value of the second virial coefficient for comblike branched polymers of various structures have recently appeared [80,81].

This result, allowing for Zimm–Klib calculations, agrees with the results of Krigbaum and Trementozzi [56], who suggested that for polymers of equal molecular weight the relation

$$(A_2)_b/(A_2)_l \cong \frac{[\eta]_b}{[\eta]_l} \tag{78}$$

is valid.

The experimental results [44,56] show that this relation is well confirmed for polymers with a narrow MWD. Hence the second virial coefficient is also somewhat sensitive to branching, like the value of the characteristic viscosity, but a more reliable theoretical basis and accuracy of measurements makes a study of the hydrodynamic parameters preferable.

A qualitative index of the presence of long-chain branching is the increased value of the Huggins constant K' in the equation for the concentration dependence of viscosity:

$$\eta_{sp}/c = [\eta] + K'[\eta]^2c. \tag{79}$$

For linear monodisperse polymers in a θ-solvent $K' = 0.5$; an improvement in the solvent leads to a decrease in K' and branching to an increase [72]. Therefore the presence of branching at a given K' is best judged by using a θ-solvent. For branched polymers of polystyrene [44,45], poly(vinyl chloride) [73], polybutadiene [74], polyacrylonitrile [75], poly(vinyl acetate) [76], etc. in corresponding "poor" and especially in θ-solvents systematic increasing in the values of K' are observed, whereas in "good" solvents this regularity does not always appear [77,78] and evidently is masked by the effect of polydispersity and volume effects. The relation between K' and branching has not been studied much theoretically, therefore this method remains purely qualitative.

It has similarly been shown [68,79] that the concentration dependence of the sedimentation constant of branched macromolecules is weaker than that of linear ones. An attempt has also been made to qualitatively characterise branching with the aid of the dynamo-optical constants of flow birefringence [59].

Determination of the polydispersity index M_w/M_n can also serve as a criterion of branching. However, the use of the value of M_w/M_n for a quantitative characteristic of branching is justified only in those instances where the branching reaction leads to the production of polymers with a given type of MWD, as for example, in the processes considered by Beasley [35], Stockmayer [31], or Bamford [37]. In the remaining instances when polymers are formed with $M_w/M_n > 2$ and it is known earlier that reaction take place leading to the formation of branched chains, use of the polydispersity index is possible only for qualitative and comparative estimates.

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The theoretical principles and experimental methods at present available permit in several instances a qualitative characterisation of the branching of various polymers. However, several problems need further attention. The principal ones are as follows: (1) the development of the theory of characteristic viscosity and of the coefficient of translational friction for branched polymers having an appreciable long-chain branching density; (2) the development of methods allowing long-chain and short-chain branching to be differentiated; (3) the synthesis and investigation of comblike branched polymers of known structure with long side-chains; and (4) a deeper study of polydisperse branched polymers.

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