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Topological structure and relaxation properties of branched polymers

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Abstract. Topological structures of branched polymers, including weakly and highly branched chains, star-shaped, H and pom – pom polymers, dendrimers and comb-like, hyperbranched and critically branched polymers, are characterised. Experimental data on their rheological and relaxation properties are analysed. Theoretical approaches to the description of relaxation spectra of branched polymers are outlined. The bibliography includes 272 references.

I. Introduction

The relaxation properties of polymers are to a large extent determined by their architecture.[1] Nevertheless, such factor as branching that influences large-scale relaxation has received much less attention than the molecular mass distribution (MMD). However, the branching factor has attracted considerable interest in recent years [2] due to the fact that the scope of synthesis of branched-chain polymers with desired topological structures has been widened.[3 – 5]

In recent years, the line of investigation associated with the synthesis of hyperbranched (superbranched) polymers (HBP) has been extensively developed in polymer chemistry and technology.[5 – 13] This interest is due to the fact that hyperbranched polymers have unique properties. Nanosized HBP particles are soluble in virtually all media and have a high sorption capacity.[14] Due to this fact, HBP have found wide use in technology (polymeric and construction materials, paint and varnish production, organic glasses, nanocomposites, *etc.*), electronics and microelectronics (polyelectrolytes, semiconductors, polymeric plasmons, *etc.*), chemistry (nanosized reactors), medicine (pharmacological nanocontainers) and ecology (sensitive environmental sensors).[11, 13, 15] In the early stage of the development of science and technology of branched polymers, dendrimers, *i.e.*, polymers having highly regular topological structures (regular Cayley trees, RCT), have been considered as HBP. In scientific literature, emphasis has been given to the development of procedures for the synthesis of dendrimers [5, 6, 9] and investigation of the rheological and sorption properties [6, 10] associated primarily with the use of dendrimers as transporting agents (for example, to deliver drugs to targeted sites). Evidently, the synthesis of dendrimers is a very complex problem because a stepwise increase in the number of generations is required to meet the condition of regularity of the structure.

In recent years, studies on the synthesis of HBP by conventional methods of polymer chemistry, *i.e.*, by polycondensation and polymerisation, have been extensively carried out.[11, 12] The resulting topological structures are less regular than those of dendrimers (irregular Cayley trees, ICT). Macromolecules formed by these methods are characterised by a broad molecular mass distribution and a broad distribution oevr the number of peripheral branches. Nevertheless, the desired properties of these macromolecules are only slightly worse than those of dendrimers and such macromolecules are relatively cheap due to a low cost of the starting materials and the simple synthesis technology.

The relaxation properties of dendrimers were studied in sufficient detail both experimentally [6, 16 – 24] and theoretically.[25 – 34] However, studies on the relaxation properties of HBP with an irregular topological structure are scarce. A knowledge of these properties can apparently be obtained by analysing the published data on the influence of branching of polymer chains on their relaxation behaviour. In other words, the relaxation properties of weakly and randomly branched polymers, star-like, comb-like, H and pom – pom polymers and critically branched polymers formed in the vicinity of the gel point are of considerable interest. This problem is dealt with in the present review.

II. Architecture of branched macromolecules

The following topological types of branched polymers were described in the literature.

1. **Randomly branched polymers**. The branching number can vary so that macromolecules can be both weakly and highly branched. This type of polymers is characterised by the branching number per chain or per a particular chain length and the average molecular mass of branches. In essence, the topological structure of branched macromolecules is ICT. Each numbered branch (starting from one end of the main chain) belongs to a particular generation. The structures of these chains are determined by the kinetics of the process of their formation, in particular, by the kinetics of the chain transfer reaction through the polymer (as in the case of radical polymerisation of ethylene or vinyl acetate).

2. **Comb-like polymers** are formed if side chains (which can be rather long) are attached to the main chain more or less regularly.

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Generally, the functionality of the branching points (f) is three. However, comb-like macromolecules with $f = 4$ ('centipedes') and $f = 6$ ('barbed wire') are also known. Polymeric molecules with densely attached side branches are considered as one-dimensional polymers (cylindrical brushes).

3. **Star-shaped polymers** are characterised by the number of branches (arms) coming from a single centre, the functionality and the molecular mass of branches (M_a). It is generally assumed that all branches have the same length. Asymmetric three-arm stars are sometimes called T polymers (two short arms and one long arm) and Y polymers (one short and two long arms).

4. **H polymers**. By H polymers are meant chains carrying two branches of equal length at each end. These polymers can be characterised by the following two parameters: the molecular masses of the chain and branches.

5. **Pom – pom polymers** are structurally analogous to H polymers with the difference that the number of branches at both ends is larger than two. Hence, these polymers are characterised by an additional structural parameter, *viz*., the number of branches at each chain end.

6. **Dendrimers** are star-shaped (in some publications (see, for example, Refs 25, 27 and 34) these polymers are called 'starbursts'). However, branches coming from the centre belong to the first generation. The arms are branched at the ends to form the second generation of branches, which, in turn, are branched at ends to form the third generation, *etc*. If the first generation consists of f_0 branches and each branch point generates f branches in the next generation, the total number of branches in the kth generation is

$$p_k = f_0 f^{k-1}.$$

The total number of branches in a macromolecule consisting of G generations is

$$P_G = \sum_{k=1}^{G} p_k = f_0 \frac{f^G - 1}{f - 1}. \quad (1)$$

7. **Hyperbranched polymers**. The above-described polymer structures are, in essence, HBP. However, since these structures are commonly called dendrimers, the term HBP will be used in reference to tree-like macromolecules with irregular structures (ICT topological structures), which are prepared by conventional polymerisation or polycondensation methods.

The structures of HBP, unlike those of dendrimers, were not unambiguously determined. Hence, *a priori* conclusions about the structures of such polymers can be drawn based on the characteristic features of the mechanism of their formation. Polycondensation of AB_f-type oligomers, for which f is generally equal to 2, is the simplest (from the kinetic point of view) industrial synthesis of HBP.[13] This process was theoretically studied by the Flory method of combinatorial analysis.[35] More recently, various statistical[36–51] and kinetic methods, including computer simulation,[49,52–63] have been used to calculate the MMD function.

In the absence of cyclisation, HBP macromolecules prepared by the above-mentioned method contain one unreacted functional group of type A and $(fn-n+1)$ functional groups of type B (n is the number of monomeric units in the molecule). Hence, the degrees of conversion at these groups (α_A or α_B, respectively) are related to each other by the following equation

$$\alpha_A = f\alpha_B.$$

The distribution function over groups B is determined by the equations

$$\langle b\rangle_n = (f-1)\,\overline{P}_n + 1,$$

$$\langle b\rangle_w = \frac{(f-1)^2\,\overline{P}_w\,\overline{P}_n + 2(f-1)\,\overline{P}_n + 1}{1 + (f-1)\,\overline{P}_n},$$

$$\frac{\langle b\rangle_w}{\langle b\rangle_n} \approx \frac{\overline{P}_w}{\overline{P}_n},$$

where the average degrees of polymerisation (in the absence of the substitution effect, *i.e*., calculated statistically) are as follows:

$$\overline{P}_n = (1-\alpha_A)^{-1},$$

$$\overline{P}_w = \frac{f - \alpha_A^2}{f(1-\alpha_A)^2},$$

$$\frac{\overline{P}_w}{\overline{P}_n} = \frac{f-\alpha_A^2}{f}\,\overline{P}_n = \frac{1}{f}(1+\alpha_A) + \frac{f-1}{f}\,\overline{P}_n.$$

It is evident that both the average degrees of polymerisation and their ratio characterising the width of the molecular mass distribution and, correspondingly, the distribution over functional groups B increase indefinitely with increasing degree of conversion.

An alternative method of calculation of MMD for hyperbranched polymers based on the principles of percolation theory[64] was developed in Ref. 59. If an HBP macromolecule is represented as a critical cluster, the distribution function (*i.e*., the fraction of molecules containing n monomeric units) is described by the equation

$$p_n \cong n^{-\tau} f\left(\frac{n}{n_{max}}\right),$$

where, according to the percolation theory,[65] $\tau = 3/2$, $f \sim \exp(-n/n_{max})$, $n_{max} \sim (1-\alpha_A)^{-1/\sigma}$, $\sigma = 1/2$. For HBP, the distribution function takes the following form:

$$p_n = \begin{cases} \dfrac{n^{\tau-2}}{\Gamma(\tau-2,\beta)}\exp\left(-\dfrac{n}{n_{max}}\right) & \text{at } n_{min} < n < n_{max}; \\ 0 & \text{at } n_{min} > n > n_{max}, \end{cases}$$

Γ is the incomplete gamma function, and $\beta = n_{min}/n_{max}$.

The so-called Frey parameter[65] or the degree of branching (DB), which is equal to zero† for linear polymers and equal to unity for ideal dendrimers, is used for topological characterisation of more complex systems (for example, of those prepared by polycondensation $AB_f + B_g$ or polymerisation). For systems consisting of AB_2-type oligomers, this parameter is equal to the ratio of twice the number of branching units (d) to the sum of twice the number of branching and linear units (l)

$$DB = \frac{2d}{2d+l}.$$

For oligomers AB_f,

$$DB = \frac{fd}{fd+l}.$$

Finally, in the general case, including various polymerisation methods of synthesis (and not only of HBP),

$$DB = \frac{d+t}{d+t+l},$$

where t is the number of end units. As an example, let us mention the results of the study,[66] where the structure of commercial HBP 'Boltorn', which was prepared by polycondensation of 2,2-bis-(hydroxymethyl)propionic acid with pentaerythritol as the central core, was examined. Due to the statistical character of the process, the macromolecules contained all three types of fragments (Table 1).

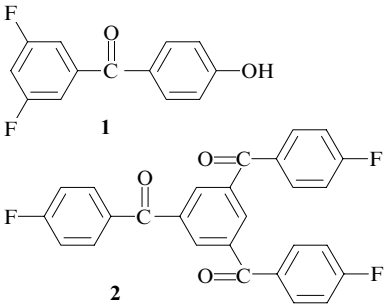
† To be more precise, $2/P_n \approx 0$.

Table 1. Characteristics of HBP 'Boltorn'.[66]

$\langle P\rangle_n$	d (%)	t (%)	l (%)	DB
16.68	13.5	28.5	58.0	0.42
21.37	16.5	26.5	57.0	0.43
61.36	17.5	23.5	59.0	0.41

Evidently, variations in either the structure [67] or concentration in the central core [68] will lead to changes in the degree of branching.

For example, it was demonstrated [68] that DB for the polycondensation product of compound **1** is 0.49, whereas DB are 0.62 and 0.67 for copolycondensation of compounds **1** and **2** in **2**:**1** molar ratios of 1:57 and 1:28, respectively.



The topological structure of HBP is determined by the kinetic parameters of the processes of their formation. In a number of studies,[54, 56] the degree of branching was demonstrated to be dependent on the ratio of the kinetic constants of the first (k_1) and second (k_2) addition, *i.e.*, on the substitution effect, even in the simplest case of polycondensation of AB_2-type oligomers. In the case of $k_1 = k_2$, *i.e.*, in the limit, at $\alpha_B = 1$, DB is 0.5. The degree of branching increases and approaches unity as the $k_2:k_1$ ratio increases; and DB decreases as this ratio decreases. In other words, the positive substitution effect results in that HBP are similar in the branching parameter to dendrimers, although the topological structure of HBP corresponds to ICT due to the statistical character of the process. In the case of the negative substitution effect, HBP have an architecture of linear polymers. The results of kinetic analysis of the structure of a model polymer (a computer model) performed in the study [49] are given in Table 2. The structure of the macromolecule was expressed in terms of the relative concentrations of the diads of the monomeric units of different types: branching units containing both reacted groups B, end units containing both unreacted groups and middle units containing one reacted group B.

Table 2. Influence of the ratio of the kinetic constants of the first and second addition on the characteristics of the structure of a model polymer.[49]

Parameter [a]	$k_1:k_2 = 1:1$	$k_1:k_2 = 1:0.1$	$k_1:k_2 = 1:10$
$l-t$	0.125	0.065	0.047
$l-l$	0.250	0.715	0.012
$l-d$	0.125	0.065	0.047
$d-t$	0.125	0.012	0.399
$d-l$	0.250	0.131	0.096
$d-d$	0.125	0.012	0.399
T	0.250	0.078	0.447
L	0.500	0.844	0.106
D	0.250	0.078	0.47
DB	0.50	0.156	0.894

[a] T, L and D are the fractions of the monomeric units t, l and d, respectively.

Polycondensation of monomers, such as *p*-chloromethylstyrene (inimers),[69] in the presence of a polyfunctional initiator is a prominent example of the influence of the kinetics of the formation of HBP on their structure. It was demonstrated [70, 71] that the polydispersity and the degree of branching of the product can be changed by varying the rate of addition of the monomer into a reactor.

The cyclisation reaction has a substantial effect on the topological structure of HBP.[53, 54, 72, 73] For example, polycondensation of 2,2-bis(hydroxymethyl)propionic acid was demonstrated [53] to afford macromolecules containing rings that are formed as a result of the intramolecular reaction of the acidic and hydroxy groups (Table 3).

Table 3. Mole fractions of poly[2,2-bis(hydroxymethyl)propionic acid] macromolecules containing rings at different degrees of conversion (α_A) and degrees of polymerisation (n).[53]

n	$\alpha_A = 0.840$	$\alpha_A = 0.947$	$\alpha_A = 0.981$
4	0.15	0.30	0.48
5	0.30	0.47	0.60
6	0.39	0.46	0.83
7	0.28	0.47	0.75
8	0.29	0.42	0.75
9	0.34	0.66	0.77
10	0.27	0.61	0.74
11	0.24	0.48	0.68
12	0.29	0.63	0.87
13	–	0.64	0.92

As can be seen from Table 3, the molar fraction of macromolecules containing rings is virtually independent of the degree of polymerisation (the exception is the tetramer) but noticeably increases with increasing degree of conversion. It should be noted that cyclisation substantially limits the average degree of polymerisation so that $\overline{P}_w$ is finite even at $\alpha_A = 1$. This fact was confirmed experimentally [73] in the study of siloxysilane-based HBP of types AB_2, AB_4 and AB_6 and theoretically by the results of kinetic calculations and computer simulation.[53, 54, 74] The in-depth study of polycondensation of oligomers AB_2 and AB_4 by the Monte Carlo method demonstrated [74] that, in the limit, all macromolecules contain rings of which more than 80% are the simplest rings, so that the average ring size for these oligomers is 1.65 and 1.39, respectively. In this case, the maximum average degrees of polymerisation are 10.7 and 7.5, respectively.

The fact that the structural characteristics (DB, $\overline{M}_n$ and $\overline{M}_w$) of commercial HBP 'Boltorn H40' differ substantially from the corresponding values calculated by probability methods is attributed [75] to the influence of various kinetic factors. Evidently, these factors have a more pronounced effect in the polymerisation method of synthesis of HBP. For example, the width of MMD in the case of radical copolymerisation of methyl methacrylate with ethylene glycol diacrylate (the molar ratio is 100:15) in the presence of dodecylmercaptan as a chain-transfer agent substantially depends on the concentration of the latter (Fig. 1). Both the ratio $\langle\overline{M}\rangle_w/\langle\overline{M}\rangle_n$ and $\langle\overline{M}\rangle_w$ exponentially decrease with increasing concentration.[76]

When considering the properties of branched polymers, the following fact should be taken into account. Weakly branched macromolecules, such as polymers with rarely attached side branches, H polymers and stars with a small number of arms, are characterised by the absence of intramolecular steric hindrance so that all branches adopt a Gaussian conformation. Comb-like polymers, stars with a large number of arms, dendrimers and HBP are characterised by intramolecular steric hindrance and only peripheral fragments of their chains can adopt a Gaussian conformation. These macromolecules consist of a core with an extended conformation of the chains and low-mobility monomeric units and the peripheral shell with the

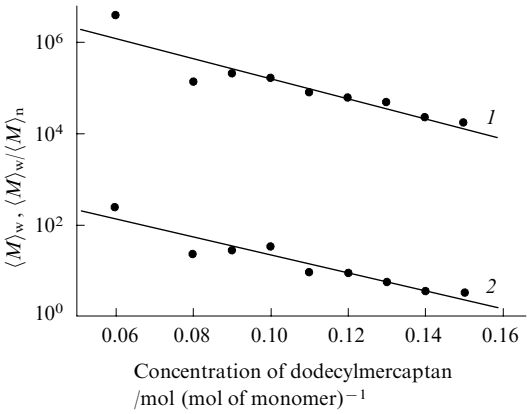


Figure 1. Plot of the parameters of the topological structures of HBP prepared by radical copolymerisation of methyl methacrylate with ethylene glycol diacrylate in the presence of dodecylmercaptan as the chain-transfer agent *vs.* the concentration of the latter.[76]
(*1*) $\langle\bar{M}\rangle_w$, (*2*) $\langle\bar{M}\rangle_w/\langle\bar{M}\rangle_n$.

Gaussian conformation of the chains and flexible monomeric units.[25,77,78] According to theoretical [79] and experimental [80] data, peripheral chains are somewhat extended.

The presence of this heterogeneous structure is reflected in the ratio of the hydrodynamic radius of the macromolecule (R_h) to the radius of gyration (R_g)

$$\rho = \frac{R_h}{R_g}.$$

This parameter quantitatively characterises the average density of monomeric units in the globule formed by the polymer.[81] For example, $\rho = 1.291$ for a dense sphere, $\rho = 0.73-0.78$ for linear polystyrene, and ρ is 1.043 and 0.971 for $\sim$50-arm stars containing branches with a molecular mass of 10^4 and 2×10^4, respectively. A decrease in the average density with increasing length of branches is evidently associated with the change in the ratio of the volume of the core to the volume of the shell.

Study by pulsed NMR spectroscopy demonstrated [78] that hyperbranched poly(ether ketones) have a heterogeneous structure. Two correlation times are indicative of the presence of a solid core and a loose shell.

The solid-like structure of the core of 3-ethyl-3-(hydroxymethyl)oxetane-based HBP is evidenced by the results of the study of the value and structure of the free volume by the positron annihilation method.[82] The free volume increases with increasing DB, whereas the glass transition temperature decreases. At the same time, the presence of a solid-like structure (paracrystalline structure according to the classification proposed in the study [82]) with a certain distribution of the free volume over holes is detected even at temperatures higher than T_g.

Due to interactions between branches, the rigidity of comb-like macromolecules increases,[83,84] so that such polymers adopt an extended conformation even in θ conditions.[85]

8. **Critically branched macromolecules** (critical clusters). The formation of cross-linked polymers by all methods (polycondensation, polymerisation or cross-linking) is accompanied by a substantial increase in the molecular mass and broadening of MMD as the conversion approaches the critical value α_c (the gelation point).[35,86–88] For example, experiments demonstrated [89] that polycondensation leads to an exponential increase in the molecular mass in the vicinity of α_c

$$\bar{M}_w \propto |\alpha_c - \alpha|^{-\gamma},$$

where $\gamma = 1.8 \pm 0.3$. According to the mean-field theory,[35] $\gamma = 2$, whereas $\gamma = 1.74$ according to the percolation theory.[64] Once the gel point is achieved, an infinite cluster is formed,[90,91] and then this cluster is transformed into a gel fraction. After gel point is attained, the width of MMD of the components of the finite-size sol fraction decreases.[86,88] Therefore, polymers have a specific topological structure at the gel point, and this structure is characterised in terms of the formalism of fractal geometry.[64,92] The fractal dimensionality of the cluster (D_f) determines the relation between the volume and the mass

$$R \propto M^{1/D_f},$$

where R is the radius and M is the mass of the cluster. It is known [93,94] that $D_f = 2$ for linear 'bodyless' chains, and $D_f = 5/3$ if the excluded volume effect is taken into account. According to the percolation theory,[64,92] $D_f = 2.53$ in the critical conversion region. Consequently, branched macromolecules have smaller volume in this region compared to linear chains.

III. Rheological properties

The viscosity (η) of melts of linear polymers is related to their molecular masses in a complex way. Low-molecular-weight compounds are characterised by a linear dependence, whereas macromolecules whose molecular masses are larger than the critical value (M_c) are characterised by an exponential dependence, the exponent being generally taken equal to 3.4 ± 0.2 (see Refs 94–96) (in the studies,[97–99] this exponent was found to be 4). The change in the type of the dependence is attributed to the formation of a entangled network accompanied by a change in the type of motion of macromolecules (from free to reptation).[94–96] The average molecular mass of entangled networks is expressed by the equation

$$M_e = \frac{M_c}{2}.$$

According to the classical reptation theory,[95,96]

$$\eta \propto M^3,$$

but this relation is true only for very large molecular masses ($M \gg M_c$). In particular,[99] for 1,4-polyisoprene $M > 2\times10^5$, whereas $M_c = 1.35\times10^4$.

It is known [86,100–102] that the viscosity of polymers is described by the dependence

$$\eta \propto [\eta]^v \text{ or } \eta \propto R^v,$$

where $[\eta]$ is the characteristic viscosity, the exponent $v \approx 6-7$, and R is the rms radius of the globule. The validity of this relation was experimentally established for different types of polymers, such as linear polymers with different degrees of rigidity, cyclic polymers, star-shaped polymers with different branch numbers, H polymers, comb-like polymers, randomly branched polymers and cross-linked polymer globules.[103–107]

Therefore, if the viscosity is considered as a function of the globule size (an argument), it is independent of the topology of the polymer. However, the globule size is very sensitive to the chain structure.[94,108–116] For macromolecules with equal molecular masses, the larger the branching in the macromolecule, the smaller the rms radius of the globule. The shrinkage factors g for multifunctional stars, *i.e.*, the ratios of the characteristic viscosities of star-shaped and linear polymers with equal molecular masses under θ conditions, are given as an example in Table 4.

There is evidence that the ratio of the radius of gyration of a macromolecular star to the radius of gyration of a branch increases depending on the functionality only to $f \approx 6$ and remains unchanged upon a further increase in f.[117] This is also true for stars with a polydisperse length distribution of branches.

In the study,[118] branched polyethylene macromolecules were synthesised and their topological structures were determined. These macromolecules were demonstrated to be A_2B-type three-arm stars (T polymers), pom–pom and comb-like polymers. The following equations were demonstrated to be fulfilled with high accuracy.

Table 4. Dependence of the size of a globule formed by stars on their functionality (the number of arms).

Polymer	Solvent	T/°C	f	g	Ref.
Polystyrene	Cyclohexane	35	3	0.78	111
			4	0.63	111
			6	0.46	111
			12	0.275	112
Polybutadiene	Dioxane	26.5	32	0.151	113
			64	0.092	114
			270	0.06	115
Polyisoprene	Dioxane	34	4	0.65	111
			6	0.46	111
Polytetrahydrofuran	THF	25	3	0.81	116
			6	0.64	116

For stars,

$$g = 1 - \frac{6s}{(s+2)^3} = 1 - \frac{3}{2}\mu(1-\mu)^2,$$

where s is the ratio M_A/M_B, $\mu = M_A/M$, and M is the molecular mass of the polymer.

The plot $g(\mu)$ is a curve with a minimum, the minimum value $g = 7/9$ corresponding to a star with equal arms. At $\mu = 0$ and 1, g is equal to unity, because a linear chain is formed in both cases.

For pom–pom polymers,

$$g = \mu^3 + 3\mu^2(1-\mu) + \frac{3}{2}\left(\frac{f+1}{f}\right)\mu(1-\mu)^2 + \frac{3f-1}{2f^2}(1-\mu)^3,$$

where $\mu = M_0/M$, M_0 is the molecular mass of the main chain, and f is the functionality of the branching point.

For comb-like polymers,

$$g = \mu^3 + \frac{2p+1}{p+1}\mu^2(1-\mu) + \frac{p+2}{p}\mu(1-\mu)^2 + \frac{3p-2}{p^2}(1-\mu)^3,$$

where $\mu = M_0/M$ and p is the number of side branches.

In the last-mentioned two cases, the plots $g(\mu)$ are monotonic curves. As $\mu \to 1$, the functions $g(\mu)$ tend to unity. When $\mu \to 0$, *i.e.*, when most of the polymer mass is in branches, these functions tend, respectively, to

$$g = \frac{3f-1}{2f^2} \quad \text{and} \quad g = \frac{3p-2}{p^2}.$$

It should be noted that the latter equation is not fulfilled for comb-like polymers based on polystyrene [119, 120] and poly(α-methylstyrene).[121]

An ellipsoid shape typical of linear macromolecules is transformed into a spherical shape in the case of symmetric star-shaped polymers, the asphericity decreases with increasing number of arms.[122]

In the presence of branches, the characteristic viscosity depends more weakly on the molecular mass [the Mark–Kuhn–Houwink (MKH) equation]. For example, the $[\eta]$ functions (tetrahydrofuran, 30 °C) of the molecular mass of polystyrene with different topological structures take the following form:[81]
for linear polymers,

$$[\eta] = 9.6 \times 10^{-5} \bar{M}_w^{0.73},$$

for 8-arm stars,

$$[\eta] = 1.42 \times 10^{-4} \bar{M}_w^{0.68},$$

for polymers with the number of arms > 20,

$$[\eta] = 6.45 \times 10^{-4} \bar{M}_w^{0.39}.$$

Dendrimers are characterised by an even weaker dependence. For example, the exponent in the MKH equation for a propyleneimine-based polymer containing the diaminobutane core and for a polyamidoamine-based polymer is 0.235 [123] and 0.05,[124] respectively.

Theoretical analysis of the dynamics in dendrimers demonstrated [27] that the characteristic viscosity linearly depends on the number of generations (calculations were performed up to the seventh generation). A linear dependence was found also for HBP prepared by polycondensation of 2,2-bis(hydroxymethyl)propionic acid with tetrafunctional ethoxylated pentaerythritol as the central core.[125] It should be taken into account that the notion of generation for HBP is arbitrary and implies not the macromolecular structure but the composition of the reaction mixture. The first generation is formed when the reactants are used in a molar ratio of 1 : 4; the second generation, in a molar ratio of 1 : 12; the third generation, in a molar ratio of 1 : 28, *etc*. [see Eqn (1)]. As opposed to dendrimers, the width of MMD for HBP increases with increasing number of the generation (Fig. 2). Figure 2 shows also the dependences of the characteristic viscosity and the exponent (a) in the MKH equation *vs*. the number of generations. Evidently, it is the increase in the polydispersity of HBP that leads to an increase in the two last-mentioned characteristics.

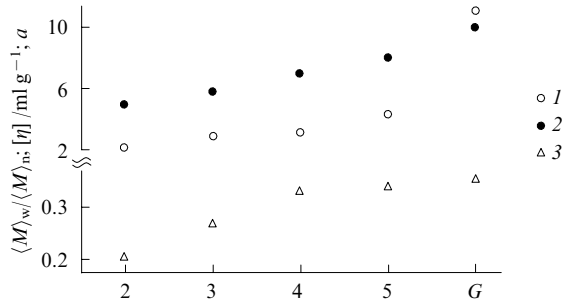


Figure 2. Dependence of the parameters of the topological structure of HBP prepared by polycondensation of 2,2-bis(hydroxymethyl)propionic acid on the number of generation.[123]
(*1*) $\langle\bar{M}\rangle_w/\langle\bar{M}\rangle_n$, (*2*) $[\eta]$, (*3*) the exponent in the MKH equation.

Study of the structures of dendrimers [33] by Monte Carlo computer simulation using the bond fluctuation model [126, 127] demonstrated that the hydrodynamic radius of the macromolecule almost linearly increases with increasing number of the generation G, whereas the analogous plot of the characteristic viscosity is a curve with a maximum (Fig. 3). These results are in agreement with experimental data [128] for dendrimers based on 3,5-dihydroxybenzyl alcohol with 1,1,1-tris(4-hydroxyphenyl)ethane as the central core. The non-monotonic character of the curve $[\eta] = f(G)$ was found also in the studies.[32, 129–132]

However, there is experimental evidence for the absence of the maximum in the plots of $[\eta]$ *vs*. the number of the generation.[133–135] Data for a polybutylcarbosilane dendrimer [135] presented in Fig. 3 (straight line *3*) serve as an example.

The non-monotonic character of the dependence under consideration is due to a change in the fractal dimension of the macromolecule as the number of generations of the dendrimer increases. The authors believe [132] that the behaviour changes from being of polymer type to colloidal type. Actually, as can be seen from the results of the study [33] presented in Fig. 4, the density distribution of monomers in the bulk of the globule becomes more uniform (excluding the central core) with increasing G. Analogous results were obtained in the study [32] by molecular dynamics. Analysis of the ratio of the radius of gyration of the globule R_g

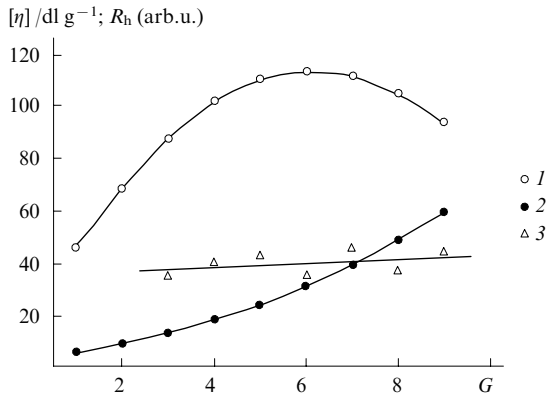


Figure 3. Plots of the characteristics of a dendrimer globule on the number of generation.
(*1*) [η], (*2*) the hydrodynamic radius R_h (computer simulation data [33]), (*3*) [η] $\times 10^3$ (results of the study [135]).

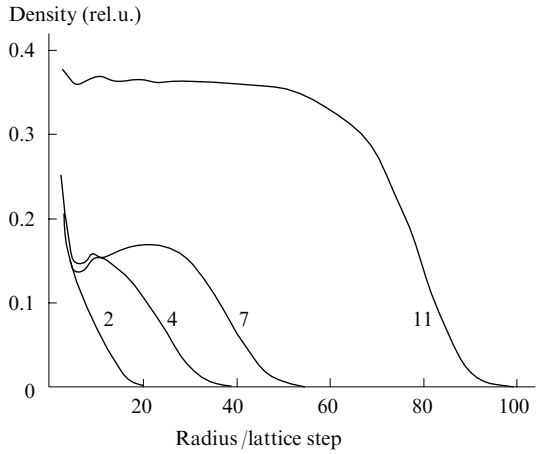


Figure 4. Density distribution of monomeric units in the bulk of a dendrimer globule based on computer simulation data.[33]
The numbers of generations are given above the curves.

formed by different dendrimers to the hydrodynamic radius R_h depending on the number of generations G demonstrated [24] that this ratio varies from 1.17 (typical of Gaussian chains) to 0.77 (characteristic of a solid sphere). In other words, the average density of monomeric units in macromolecules increases with increasing globule size.

However, the character of the density distribution depends to a large extent on the following factors: the degree of intermolecular interactions between branches,[133] the exclusion volume [136] and the flexibility of branches.[137] In the absence of an extreme dependence, polymers are characterised by high density, which is the same for different generations (this fact was demonstrated in the study [135]). In other words, in these cases dendrimers of all studied generations exhibit properties of colloidal rather than polymeric particles.

As for HBP, an analogous dependence for the characteristic viscosity was found by computer simulation.[138] To our knowledge, direct experimental evidence is lacking.

Branched chains are characterised by a complicated thermorheological behaviour [107, 139–149] due to the fact that the effective energy of viscous flow of branched polymers (unlike that of linear polymers) depends on the molecular mass, MMD and the degree of branching. It is even proposed to use these dependences for the determination of weak long-chain branching, which cannot be revealed by other methods.[148] For example, the temperature dependence of the viscosity of a low-density polyethylene melt characterised by long-chain branching was demonstrated [150] to be a function of MMD. The effective activation energy (E_a) of flow increases from 25.5 to 36.8 kJ mol^{-1} as the polydispersity index $\langle M\rangle_w/\langle M\rangle_n$ changes from 3.3 to 12.7.

Analogous results were obtained for polycarbonate.[151] The temperature dependence of flow of linear polycarbonate is determined by $E_a = 109$ kJ mol^{-1}, whereas $E_a = 121$ kJ mol^{-1} for a branched polymer ($\sim$0.7 branchings per chain) with approximately the same molecular mass and the polydispersity index.

The relationship between E_a and the degree of branching L ($L < 1$ per 10^4 carbon atoms of the polyethylene chain) is represented by the relation:[147]

$$E_a \propto \bar{M}_w^2 L.$$

It was demonstrated [152] that

$$E_a \propto \log \bar{M}_w,$$

if the polyethylene chain adopts a configuration of three- or four-arm symmetric and asymmetric stars as well as of H- and comb-like (up to 30 branches) polymers.

The prevailing opinion is that the thermorheological effect is associated with the globule size. It is suggested that the influence of the temperature on the viscocity is determined not only by the temperature dependence of the friction coefficient but also by the temperature coefficient of the globule size [153]

$$\kappa = \frac{d\ln\langle r^2\rangle}{dT},$$

where $\langle r^2\rangle$ is the rms radius of gyration of the macromolecule. The coefficient κ increases with increasing degree of branching.[107, 142, 143] As a consequence, the effective activation energy of viscosity also increases.

Graessley hypothesised [139] that the part of the activation energy associated with the branching effect is related to the branch length by the equation

$$E_b = \Lambda \frac{M_a}{M_e},$$

where Λ is the coefficient dependent on the chemical structure of macromolecules and the coefficient κ.

However, it appeared that the relationship between Λ and κ is rather complex and even non-correlated.[1, 154] Apparently, the nature of the thermorheological effect is not associated with the topological properties of the macromolecular globule. Actually, globules formed by macromolecules, including those formed by branched molecules,[155] in blocks have a θ size and the temperature has no effect on this parameter, as opposed to the state in dilute solutions.[94] The concentration of entanglements is also temperature independent because the entanglements are not energetic in nature.[94] However, the temperature exerts a strong effect on the concentration and the lifetime of branching points of the physical network,[156] such as nematic clusters.[157] This hypothesis is supported, for example, by the fact that the thermorheological properties are typical of polyethylene,[147, 158] which is prone to crystallisation and, consequently, to the formation of nematic clusters, but is not typical of an essentially amorphous polystyrene.[154] Therefore, the phenomenon under consideration is most likely associated with the physical network rather than with entanglements. The fact that it is necessary to take into account energy interactions was also noted in the study,[159] where a hairpin model, *viz.*, intrachain folded structures, was considered.

The characteristic viscosity of weakly branched polyethylene chains (the number of branches per 10^4 carbon atoms of the main chain < 1) is similar to that of linear chains with the same molecular mass,[160–163] but the viscosity of the former is higher.[147, 158, 161–164] For example, the region of the degrees of branching L up to 0.5 per 10^4 carbon atoms is characterised [164] by

$$\eta \propto \exp(5.6\,L).$$

An increase in the viscosity with increasing degree of branching was observed for polypropylene as well.[165]

The viscosity of polyethylene was demonstrated [152] to depend approximately exponentially on the molecular mass if the chain adopts a configuration of three- or four-arm symmetric stars, asymmetric stars or H polymers. For symmetric stars, the following relation is fulfilled:

$$\eta \propto M_a^{6.5}.$$

For asymmetric stars, no analogous relations were found.

In the study of 1,4-polyisoprene, the viscosity of three-arm stars, including asymmetric stars, was demonstrated [166] to depend on the molecular mass of the largest branch as $M^{5.9}$ (M_a/M_e was varied from 7 to 43).

For moderately and highly branched polyethylene macromolecules (the number of branches per 10^4 carbon atoms of the main chain is much larger than unity), $g < 1$. As a consequence, their viscocity is lower than that of linear macromolecules with the same molecular mass.[167] Analogous results were obtained for polypropylene (the number of branches varies from 0.8 to 7.8 per 10^4 carbon atoms)[168] and poly(methyl methacrylate) (185 branches per 10^4 carbon atoms).[169] In the former case, the viscosity decreases by a factor of ~ 50, and it decreases by more than two orders of magnitude in the latter case.

In the reptation theory of star-shaped chains,[96, 154, 170] the following equation was derived:

$$\eta \propto \left(\frac{M_a}{M_e}\right)^b \exp\left(v\frac{M_a}{M_e}\right), \qquad (2)$$

where b and v are model parameters.

Relation (2) reflects the fact that the ratio of the radius of a globule formed by star macromolecules to the radius of the branch is independent of the number of branches at $f > 6$, this relation being true for both monodisperse and random length distributions of branches.[171] Actually, it was experimentally demonstrated [172] that the viscosity of star-shaped polymers is independent of the branch number if the latter is larger than three, but the viscosity depends almost exponentially on M_a.[96, 173] The corresponding data for monodisperse star polyisoprene are shown in Fig. 5. It can be seen that the number of branches is of no significance. Polymers with small M_a (see Fig. 5 *a*) obey the power law with the exponent of 2, and polymers with large M_a (see Fig. 5 *b*) are governed by the exponential law according to Eqn (2).

The rheological properties of dendrimers with a small number of generations ($G < 4$) are similar to those of star-shaped polymers.[21, 130, 174] Due to a spherical shape and a rather close packing of dendrimers with a large number of generations, the properties of solutions and melts of such polymers are analogous to those of colloidal compounds.[19, 21, 23, 32, 130, 174, 175] The dependence of the viscosity on the molecular mass of amidoamine-based dendrimers was demonstrated [175] to be quadratic for low G and linear for high G (G varies from 1 to 7, and the molecular masses vary from 5×10^2 to 1.17×10^5). The same dependences were found for propyleneimine-based dendrimers.[19] This was confirmed by data from computer simulation by molecular dynamics.[32]

Since the topological structure of HBP can vary over a wide range, the rheological characteristics of these polymers are ambiguous. The plots of the viscosity of HBP prepared by copolycondensation of AB_2-type monomers {*N*-[3,5-di(*tert*-butyldimethylsilyloxy)phenyl]-4-fluorophthalimide} with AB-type monomers {*N*-[3-(*tert*-butyldimethylsilyloxy)phenyl]-4-fluorophthalimide} [176] *vs.* the degree of branching and $[\eta] = f(DB)$ (see Ref. 177) are presented in Fig. 6. A decrease in the degree of branching due to an increase in the fraction of linear fragments in the structure of a copolymer leads to an exponential increase in the volume of a globule formed by the macromolecules and, consequently, in the viscosity of HBP melts.

The viscosity of highly branched polymers is also described by the relation (2).[19, 173, 178, 179] It was experimentally found [96, 107, 154, 180–182] that in this case $0.5 \leqslant b \leqslant 2$, $v < 1$ (according to the reptation theory,[96] $b = 2$, $v = 15/8$).

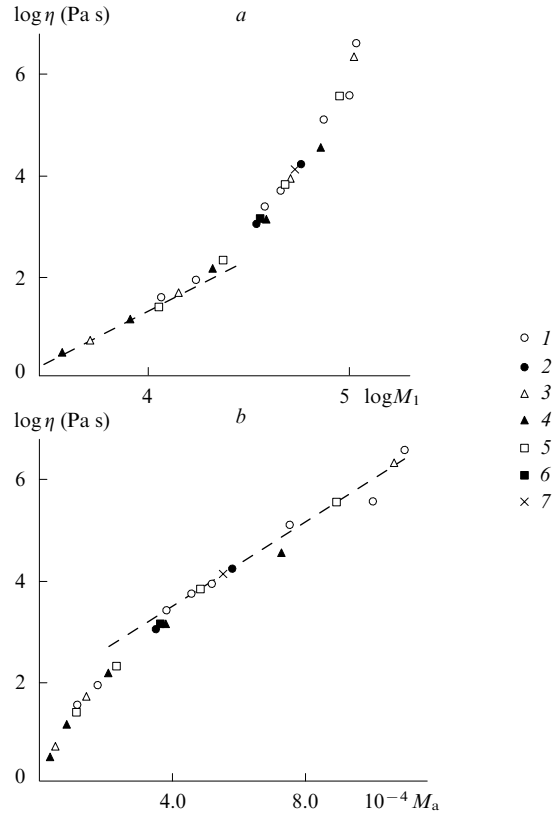


Figure 5. Plots of the viscosity of the polyisoprene melt *vs.* the molecular mass of the arm in logarithmic (*a*) and semilogarithmic (*b*) coordinates.[173] The functionality: (*1*) 4, (*2*) 5, (*3*) 8, (*4*) 12, (*5*) 18, (*6*) 27, (*7*) 33.

As in the case of linear polymers, the dependence of the viscosity of solutions and melts of branched polymers on the conditions of their deformation, *i.e.*, non-Newtonian flow is observed only for rather large molecules. At the same time, the degree of branching plays an important role. It was demonstrated [167] that the critical shear rate γ_c, which determines the region where the viscosity begins to decrease with increasing shear rate, increases with increasing degree of branching of weakly branched low-density polyethylene. These results were confirmed by the data from computer simulation by molecular dynamics.[183] Analogous results were obtained for polycarbonate.[151] For the same degree of polymerisation, star-shaped (from 3 to 6 arms),

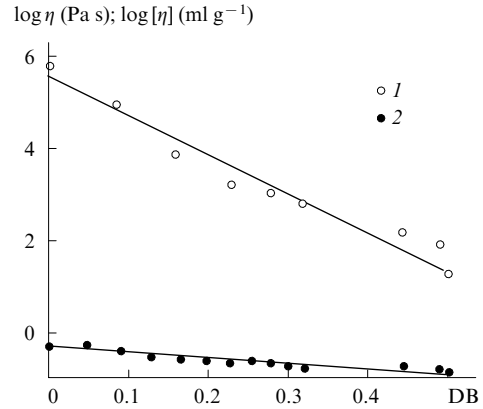


Figure 6. Plots of the viscosity of the melt (*1*) and the characteristic viscosity (*2*) of HBP *vs.* the degree of branching.[176, 177]

comb-like (from 4 to 8 branches) and H polymers are characterised by higher viscosity at high shear rates compared to linear polymers. At the same time, linear polymers are characterised by a larger difference between normal stresses. Branched polymers have a high longitudinal viscosity [184, 185] and are characterised by an increase in the viscosity with time in the course of uniaxial deformation.[168, 186–193] The higher the degree of branching the larger the increase in viscosity. Highly branched polyethylene, which was prepared with the use of the complex (Pd + diimine) catalyst, shows Newtonian flow behaviour.[194]

In studies of polyamidoamine,[21, 174] it was demonstrated that dendrimers exhibit the same properties; the smaller the number of the generation G, the larger γ_c. At $G = 1$, no decrease in the viscosity in the region of shear rates under study (approximately up to 3×10^2 s^{-1}) was observed. The effect of a decrease in the viscosity with increasing molecular mass of propyleneimine-based dendrimers and HBP having a chemical structure of ester and ester amide was found in the study.[19] The viscosity of low-molecular-weight compounds ($\bar{M}_n < 4.3 \times 10^2$) is independent of the shear rate (Newtonian flow). Melts of a dendrimer based on 2-dimethylpropionic acid up to the fifth generation inclusive [179] and a dendrimer based on polyamidoamine at low temperatures up to the sixth generation behave analogously. At higher temperatures, the viscosity depends on the shear rate, the temperature range of Newtonian flow decreasing with increasing number of the generation. For $G = 2$, Newtonian flow is retained up to 85 °C; for $G = 4$, up to 70 °C, whereas the dependence of the viscosity on the shear rate for $G = 6$ is observed already at 40 °C.[21]

The characteristic rheological features of HBP depend on their structure. Study of poly(ester amide) [195] demonstrated that the higher DB the smaller γ_c.

Hyperbranched polymers based on esters and ester imides [176] have the same properties, γ_c decreasing with increasing DB due to an increase in the fraction of an AB-type copolymer. An analogous effect was documented in the study by molecular dynamics of HBP with a variable length of linear fragments.[196]

The chemical structure of terminal groups responsible for the character of intra- and intermolecular interactions is an important factor that has an effect not only on the rheological properties of hyperbranched polymers but also on the glass transition temperature.[13] For example, the viscosities of dendrimers based on propyleneimine with terminal nitrile groups differ by an order of magnitude from those of dendrimers with terminal amino groups.[19] In the latter case, the structure of macromolecules is more compact and, consequently, the viscocity is lower due apparently to intramolecular hydrogen bonding. An HBP melt based on polyester with terminal hydroxy groups shows Newtonian flow behaviour, whereas the flow of concentrated solutions of ester imide HBP is non-Newtonian (the viscosity depends on the shear rate). The replacement of 60% of terminal hydroxy groups in HBP prepared from 2,2-bis(hydroxymethyl)propionic acid by the ester groups $O_2C(CH_2)_{10}Me$ leads to a decrease in the viscosity by more than two orders of magnitude.[125] It was demonstrated [30] that the flow of polyamidoamine dendrimers is temperature dependent. The higher the temperature, the more substantial the non-Newtonian character of flow. This phenomenon is apparently associated with a decrease in the concentration of intramolecular hydrogen bonds and formation of a labile network due to chain–chain intermolecular interactions. The possible mechanism of this process was proposed in the study.[197] It was hypothesised [198] that a substantial difference in the character of intermolecular interactions is responsible for a sharp decrease in the viscosity of melts of three-arm star polybutadienes upon the replacement of terminal dimethylamino groups by polar zwitterionic groups.

IV. Relaxation modulus

Main theories of the relaxation mechanism of branched polymers [2, 154, 199–201] are based, first, on the tube model,‡ and, second, on the hierarchy of relaxation processes.[166, 202–206] De Gennes considered diffusion of star-shaped chains in the presence of fixed obstacles and demonstrated [170] that the branching point is fixed in space and, consequently, the reptation motion is forbidden until the relaxation process to this point is not completed. In the presence of several branches, the term 'hierarchy' of relaxation is introduced,[207–209] which is determined by the relaxation time dependent on the branch length. The scheme of relaxation of branched macromolecules is shown in Fig. 7. It is suggested that the shortest branch is the first to relax, resulting in an increase in the effective friction coefficient of the main-chain unit linked to the branching point. Then the same occurs with longer branches, the longer being the branch the larger being the corresponding friction coefficients. Only once relaxation of the longest branch is completed, the reptation motion of the whole macromolecule becomes possible. When estimating the relaxation times of branches of the second and succeeding hierarchical levels, it is customary to take into account dynamic expansion of a tube due to relaxation of branches,[199] *i.e.*, the influence of the number of branches is analogous to the solvent effect. It should be noted that there is a reason [210, 211] to doubt the necessity of taking into account this effect.

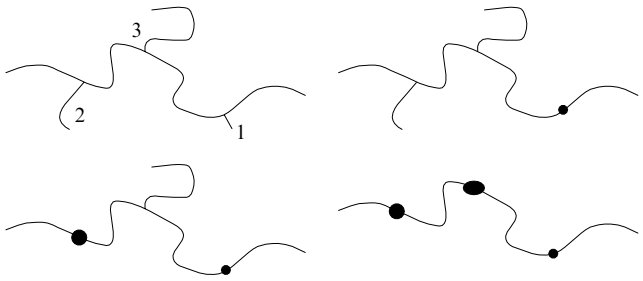


Figure 7. Scheme of relaxation of branched macromolecules, in which the branch length is larger than M_e.
The numbers at branches correspond to the hierarchical level. The size of branching points reflects the effective friction coefficient.

The concentration of fragments belonging to this hierarchical level is determined by the equation

$$c_i = N_i \frac{M_{bi}}{M_w},$$

where N_i and M_{bi} are the number of branches of the ith level and their molecular mass, respectively.

From the aforesaid, according to the publication,[212] the following hierarchy of the relaxation times of ICT can be proposed. The time required for reaching the coordinate s by the end of the chain belonging to the first hierarchical level is determined by the equation [172]

$$t_1(s) = t_0 \left[\frac{6v}{M_e M_{bl}} \left(\frac{s^2}{2} - \frac{s^3}{3M_{bl}} \right) \right],$$

‡ A tube is a region that limits the lateral motion of macromolecules, where reptation motion is possible.[94–96]

and the maximum time corresponds to the coordinate $s = M_{b1}$. Hence, for this level we have

$$\tau_1^{max} = t_0 \exp\left(\frac{vM_{b1}}{M_e}\right);$$

for succeeding levels

$$\tau_i^{max} = \tau_{i-1}^{max}\left(\frac{M_{bi}}{M_e}\right)^{1/2} \exp\left(\frac{vM_{b1}}{M_e}\right).$$

In these equations, t_0, according to the theory,[172] is the characteristic time for three-arm stars

$$t_0 = \frac{4}{3}\tau_0 \frac{M_{b1}^2}{m_0^2}\left(\frac{\pi M_e}{vM_{b1}}\right)^{1/2},$$

where v is the constant, which is equal to 0.56 for the first level and slightly changes with the hierarchical level, m_0 is the molecular mass of the monomeric unit, and τ_0 is the elementary relaxation time characterising diffusion of the monomeric unit.

For macromolecules with a functionality of branching points larger than three (star-shaped, H and pom–pom polymers), the same scheme is used for calculations of the relaxation times corrected for the fact that the branches coming from a single point are 'separated' by a zero-length main chain fragment.[208]

The relaxation modulus is determined as a sum of the contributions of all levels

$$G(t) = G_N^0 \sum_i c_i F_i(t),$$

$$F_i(t) = 2\int_0^{M_{bi}} \left[\left(\bar{c}_i - c_i \frac{s}{M_{bi}}\right)\exp\left(-\frac{t}{t_i(s)}\right)\right] ds, \qquad (3)$$

where G_N^0 is the modulus corresponding to a high-elasticity plateau, $\bar{c}_i$ is the 'dynamic' concentration of branches of the ith level,

$$\bar{c}_i = \sum_{i=k}^{N} c_k;$$

N is the total number of levels.

In experiments, Eqn (3) is manifested, in particular, in that the dependence of the length of a high-elasticity plateau $\Delta\log\omega$ (ω is the deformation frequency) on the molecular mass for branched polymers is stronger than that for linear polymers. As can be seen from the data presented in Fig. 8, the coefficient v for linear monodisperse polystyrene [213] in the relation

$$\Delta\log\omega \propto v \log M$$

is 3.5, whereas $v = 4.8$ for four-arm star polyisoprene.[214] For molecular mass ($\bar{M}_w \approx 6 \times 10^4$), the frequency dependences of the real (G') and imaginary (G'') parts of the complex relaxation modulus of linear polymers are virtually equal to those of three-arm star-shaped polymers. At the same time, the terminal region for eight-arm polymers is substantially shifted to higher frequencies, although the character of the dependences $G'(\omega)$ and $G''(\omega)$ remains the same:[178]

$$G' \propto \omega^2 \text{ and } G'' \propto \omega.$$

A complication of the topological structure of macromolecules leads to a shortening of the high-elasticity plateau. This can be seen, for example, in Fig. 9, which presents the curves of the frequency dependences of the relaxation modulus for a six-arm pom–pom polymer (three arms are attached to each end of the main chain) and an analogous polymer, which contains two branches at the midpoint of the chain, resulting in the formation of an eight-arm polymer. The molecular masses of the polymers are 2.15×10^5. The high-elasticity plateau for highly branched

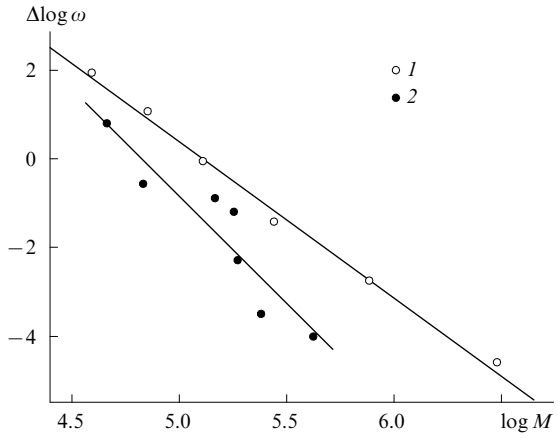


Figure 8. Plots of the length of a high-elasticity plateau *vs.* the molecular masses of linear (*1*) and four-arm star-shaped (*2*) polymers.[213, 214]

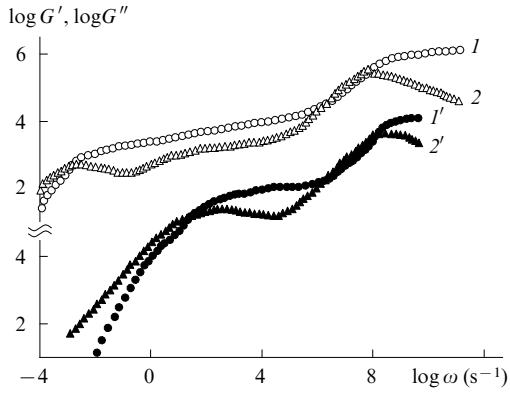


Figure 9. Frequency dependences of G' (*1*, *2*) and G'' (*1′*, *2′*) for 6-arm (*1*,*1′*) and 8-arm (*2*,*2′*) polymers.[215]

stars [178] (the branch number is ~50) virtually disappears, and in the terminal zone $G' \propto \omega^{1.12}$ and $G'' \propto \omega^{0.91}$ ($\bar{M}_w \approx 2.5 \times 10^5$); $G' \propto \omega^{1.1}$ and $G'' \propto \omega^{0.85}$ ($\bar{M}_w \approx 5.75 \times 10^5$).

It was suggested [77] that star-shaped polymers can be arbitrarily classified into two groups depending on the relaxation properties. One class includes polymers, which contain a relatively small number of long branches (or a large number of branches, but the branches are very long). These macromolecules are characterised by typical polymer dynamics. In particular, the highly elastic state is typical of such polymers. The topological structures of macromolecules belonging to another class are characterised by the presence of a large number of relatively short branches, and such polymers exhibit properties, which are more typical of colloidal systems.

An analogous behaviour is typical of macromolecules with more complex topological structures, for example, of comb-like [216] and pom–pom polymers.[217] The frequency dependence of the relaxation modulus of polymers with long branches ($M_a \geqslant 10\,M_e$) can be approximately described in terms of a theory, which is based on the above-mentioned postulates and was developed in the studies,[2, 201, 218] meanwhile this theory is inapplicable to polymers with shorter branches [$M_a \sim (2-3)\,M_e$]. In the region of moderate frequencies (a high-elasticity plateau), both G' and G'' change as $\sim\omega^{0.5}$. In the terminal region, G' is proportional to $\sim\omega^{1.5}$, and $G'' \propto \omega$. As can be seen, the above relations are not adequately described by Rouse dynamics.

An approach based on the Rouse chain model is applicable to relaxation of dendrimers.[19] The minimum number of modes

required for an adequate description of experimental data depends on the macromolecule size as follows:[21]

Number of generations of branches	< 3	4	5	6
Number of modes	1	2	9	15

However, this gives rise to a 'non-Rouse' dependence of the relaxation modulus on the frequency in the terminal zone

$$G' \propto \omega^{1.49},\ G'' \propto \omega^{0.92}.$$

A deviation from Rouse dynamics was found in the study [219] for dendrimers based on branched polystyrene. Although in this case the topological structure of macromolecules is RCT, the authors suggested that the structures of these macromolecules are analogous to those of critical clusters and, consequently, the relaxation modulus depends on the time according to a power law (see below).

In the case of HBP based on 2,2-bis(hydroxymethyl)propionic acid ($M_w = 2.6 \times 10^4$), a high-elasticity plateau is absent at all.[172] Relaxation of hyperbranched poly(ester amide) occurs according to Rouse dynamics [176, 220] if DB > 0.2 (DB was varied by changing the ratio of the comonomers AB and AB_2). For DB < 2, there is a tendency to form a high-elasticity plateau. The same relaxation mechanism was established for 5-(hydroxyalkoxy)isophthalate- [59] and ether ketone-based [68, 221] HBP. However, in these cases the Rouse law is also approximately fulfilled in the moderate frequency region, whereas it is fulfilled only for G'' but not for G' in the terminal region. It should be noted that the above relaxation characteristics should correspond to the Kargin – Slonimskii – Rouse model, *i.e.*, to linear rather than to branched chains.

Rouse dynamics and the absence of a high-elasticity plateau in the moderate and low frequency region in the case of relaxation of highly branched polymers [19, 21, 59, 68, 77, 169, 176, 219, 220] and weakly branched plyethylene [158, 161, 222] suggest that the topological structures of these compounds are similar to those of critical clusters. The fact that the structure of HBP has fractal properties (self-similarity) was demonstrated by computer simulation.[74]

The relaxation properties of a polymer system at the gel point are described by a power law [223 – 227]

$$G(t) \propto t^{-n}, \qquad (4)$$

where G is the relaxation modulus and t is the running time.

The exponent n is related to the fractal dimensionality by the equation [228]

$$n = \frac{D}{D_f + 2},$$

where D is the space dimensionality; $n = 0.66$ for a three-dimensional space and the fractal dimensionality of the critical cluster $D_f = 2.53$.

The exponent n in Eqn (4) varies depending on the system (Table 5).

If the conversion α is expressed in the form

$$\varepsilon = \left|\frac{\alpha - \alpha_c}{\alpha}\right|,$$

where ε is the relative conversion and α_c is the critical conversion, then at $\alpha < \alpha_c$ the dependence of the viscosity on ε takes the form

$$\eta \propto \varepsilon^{-s},$$

at $\alpha > \alpha_c$ the dependence of the shear modulus on ε is as follows:[229 – 234]

$$G \propto \varepsilon^{r}.$$

The exponents s and r are related to n by the equation

$$n = \frac{r}{s + r}.$$

As a consequence of Eqn (4), the frequency dependences obey a power law

$$G' \sim \omega^n \cos\left(\frac{\pi n}{2}\right),\ G,'' \sim \omega^n \sin\left(\frac{\pi n}{2}\right),$$

where $\delta = \pi n/2$. Consequently, $\tan\delta$ is frequency independent.

These relations were confirmed by numerous experiments, in particular, for three-dimensional polymerisation of methacrylate-based oligomers[235] and in the case of end-linking of polydimethylsiloxane.[236] Analogous dependences are typical of biopolymers.[237, 238] In the latter case, physical conditions, for example, the temperature, pH or concentrations of the components, are responsible for the formation of an equilibrium network. In xanthane solutions, the exponent ρ in the formula

$$\tan\delta \propto \omega^{\rho}$$

Table 5. Exponents n in formula (4) for various systems.

System	n	Ref.
Theoretical estimates	0.706	232
	0.79	241
	0.66	242
Polyethylene, number of branches per 10^5 carbon atoms		
2.6	0.711	221
3.7	0.622	221
4.2	0.589	221
8.0	0.511	221
Branched polypropylene	0.46	193
	0.53	193
Branched poly(methyl methacrylate)	0.54	167
22-Arm comb-like polybutadiene	0.55	243
Comb-like copolymer of styrene and butadiene (~30 branches)	~0.5	206
32-Arm pom – pom copolymer of styrene and butadiene	0.55	244
Hyperbranched poly(ether imide)	2/3	19
Chemical gel formation		
Cross-linking of polydimethylsiloxane	0.5	224
	0.69 ± 0.005	234
Curing of epoxy resin	0.7	245
	0.70 ± 0.02	246
	0.71	247
	0.70 ± 0.05	248
	0.5 – 0.8	249
Polymerisation of methacrylate oligomers (increases with increasing functionality)	from 0.4 ± 0.2 to 0.6 ± 0.1	235
Cross-linking of bifunctional oligodimethylsiloxane containing terminal vinyl groups by a polyfunctional reagent (f = 4 and 11) containing the reactive ≡SiH groups	from 0.69 to 0.76	236
Polycondensation of tetraethoxysilane	0.72 ± 0.03	250
Pectin + Ca^{2+}	0.71	251
Cross-linking of L-guluronic and D-mannuronic acids	0.55	252
Diisocyanate + triol + alcohol	0.73	233
Triisocyanate + diol	0.5	253
Poly(oxypropylene)triol + diisocyanate	0.69	216
Physical gel formation		
Thermoreversible triblock copolymer	0.70 ± 0.02	217
Thermoreversible microgel	0.02	254
Gelatin	0.46 – 0.70 [a]	255
Multiarm polyacrylic acid (concentration transition)	0.21	256
Crystallisation of polypropylene	0.13	257

[a] Depending on the concentration and temperature.

for complexation with Al^{3+} ions varies from -0.1 to 0.08 depending on the temperature and is equal to zero at 32 °C.[239] The exponent ρ varies approximately in the same range depending on pH, the critical pH being 2.9.

Lowering of the temperature in an aqueous-methanolic solution of spherical microgel particles of *N*-isopropylacrylamide leads to the gel – sol transformation (the lower critical temperature is 32 °C).[240] In this case, the above phenomenon is also observed, the temperature of ~29 °C corresponding to the zero value of the exponent ρ.

It should be noted that identification of the topological structures of hyperbranched polymers with those of critical clusters is arbitrary. Actually, although the dependence $G'(\omega)$ is virtually identical to $G''(\omega)$ in a moderate frequency region, their ratio, *i.e.*, $\tan\delta$, does change with frequency,[19, 59, 206] which is not typical of true fractal structures of critical clusters. If hyperbranched polymers are prepared by three-dimensional copolymerisation or chain cross-linking, macromolecules formed in the vicinity of the gelation point have structural characteristics of critical clusters, which was demonstrated by direct structural studies using gel permeation chromatography and static and dynamic light scattering.[234, 257–259]

V. Relaxation spectra

The relaxation spectrum (RS) is a universal characteristic of the relaxation properties of polymers.[1, 93, 96, 181, 260] On the one hand, analysis of theoretical models of the dynamics of polymer chains provides knowledge about RS. On the other hand, in spite of difficulties in reproducing such spectra from the results of relaxation experiments,[261–263] a comparison of RS is considered as the most adequate procedure for estimation of the validity of a theoretical approach. Since the relaxation spectrum is sensitive to the topological structure of the polymer chain,[1] branching would be expected to be reflected in the spectral pattern. However, data demonstrating the influence of branching on RS are scarce.

One of approaches is based on the use of an empirical BSW spectrum,§ which satisfactory describes the frequency dependence of the relaxation modulus of linear polymers as the following three branches: a descending branch at $\lambda \leqslant \lambda_1$, an ascending branch at $\lambda_1 \leqslant \lambda \leqslant \lambda_{max}$ and a sharply descending branch at $\lambda > \lambda_{max}$ (see Refs 225, 264 and 265)

$$H(\lambda) = \left[H_g\left(\frac{\lambda}{\lambda_c}\right)^{-n_g} + n_e G_N^0\left(\frac{\lambda}{\lambda_{max}}\right)^{n_e}\right]\exp\left[-\left(\frac{\lambda}{\lambda_{max}}\right)^{\beta}\right], \quad (5)$$

where

$$H_g = n_e G_N^0\left(\frac{\lambda_1}{\lambda_{max}}\right)^{n_e}\left(\frac{\lambda_1}{\lambda_c}\right)^{n_g}.$$

Here, λ is the relaxation time, λ_1 is the time at which two first branches coincide (intersect), λ_c characterises the segment mobility, and λ_{max} is the maximum Rouse or Doi – Edwards relaxation time depending on the conditions of realisation of the chain dynamics. As a rule, $n_g \approx 0.67$, $n_e \approx 0.30$, and $\beta = 2$.

Investigation of star-shaped polymers [266] led to a substantial complication of BSW spectra. It appeared that Eqn (5) should be supplemented with the term

$$n_0 G_0\left(\frac{\lambda}{\lambda_0}\right)^{n_0}\exp\left(\frac{\lambda}{\lambda_0}\right)^{\beta},$$

where n_0 and G_0 are constants.

Hatzikiriakos *et al.*[266] analysed the parameters of the expression for BSW spectra thus modified for a series of star polybutadienes with a regular structure with $f = 4–125$. The parameters

§ BSW are the first letters of the last names of the authors of the study.[264]

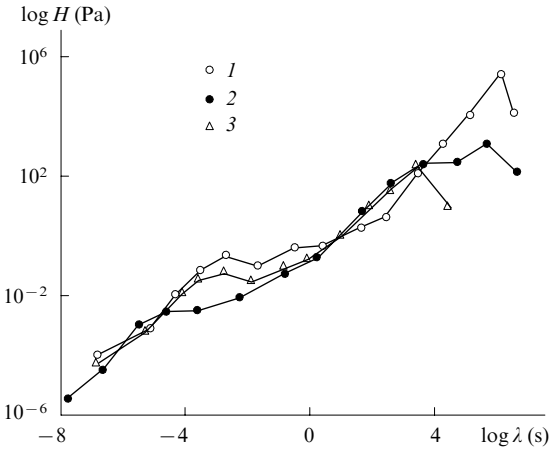


Figure 10. Relaxation BSW spectra of linear (*1*), 125-arm star-shaped (*2*) and 4-arm star-shaped (*3*) polymers.[266]

G_N^0, H_g and λ_c can be considered independent, within experimental error, of the molecular mass and the number of branches. The parameters G_0, λ_{max} and λ_1 depend more on the molecular mass of branches than on their number. The parameter λ_0 is influenced by both structural characteristics. It was suggested [266] that these results do not qualitatively contradict the theoretical concepts. The relaxation time distribution functions (BSW spectra) shown in Fig. 10 illustrate that the relaxation properties of star-shaped polymers are in fact independent of the number of branches.

At the same time, a substantial broadening of the spectrum was observed (calculations were carried out according to a procedure published in the study [267]) with increasing number of branches L in polyethylene [147, 163] in the region $L \leqslant 1$ per 10^4 carbon atoms, *i.e.*, where branching leads to an increase in the viscosity (see above).

The general approach to the solution of the problem of dynamics of chains with a complex topological structure, which generalises the Rouse model (theoretical calculation of RS) was described by Müller.[241] A macromolecule adopting an arbitrary configuration is represented as a set of N points in a d-dimensional space ($d \geqslant 2$), each point occupying the position $R_i(t)$, $i = 1, 2, \ldots, N$. The movement of these points is limited by elastic harmonic bonds, which link point units in pairs thus providing the desired architecture. The potential energy of this macromolecule is

$$U \propto \sum_{i,j}\left(R_i - R_j\right)^2.$$

In the simplest case, the relaxation dynamics is described by the equation

$$\frac{\partial U(t)}{\partial R_i} = -\zeta_i\left[\frac{dR_i(t)}{dt} - v_{ext}(R_i(t), t)\right] + \xi_i(t), \quad (6)$$

where ζ_i is the friction coefficient, v_{ext} is the external shear stress, and ξ_i is the randomly fluctuating force (thermal noise).

A somewhat different approach providing an efficient solution of Eqn (6) based on matrix factorisation and giving rise to a total RS was developed in the study.[268] The motion of elastically linked particles is described by an analogous equation system.

$$\zeta_i \boldsymbol{x}_i = \sum_j p_{ij}(x_j - x_i),\ i = 1, \ldots, n, \quad (6a)$$

where $\boldsymbol{x}_i$ is the vector of coordinates of the ith particle, and $p_{ij} = p_{ji} \geqslant 0, \zeta_i > 0$ for all i and j. The equation system (6a) is associated with a link graph of particles. The vertices i and j are linked to each other if $p_{ij} > 0$. It is reasonable to consider the

linkage components into which (in the general case) this graph is split as model macromolecules (monomeric units of the latter are essentially the graph vertices). Infinite values $\zeta_i = \infty$ can be ascribed to the friction coefficients of individual branching points in model (6a). For such branching points, $x_i = 0$, *i.e.*, branching points with infinitely large friction are fixed. Since system (6a) is split into independent differential equation subsystems corresponding to linked subgraphs of bonds, it is sufficient to study motion of an isolated macromolecule.

To take into account interchain interactions, Eqn (6) for stars and analogous structures is solved based on the reptation model.[2, 154, 200, 201, 269] For dendrimers, interchain interactions are generally ignored, and relaxation processes are attributed to intrachain conformational rearrangements.[27–31] The same is true for HBP and other polymers with topological structures of highly branched and hyperbranched ICT, which can be considered as critical clusters.[60, 256]

The parameters of RS characterising the relaxation properties of branched polymers are given in Table 6. Of the total spectrum, two relaxation times are generally distinguished: segmental and normal.[270]

Table 6. Parameters of RS characterising the relaxation properties of branched polymers.

Parameter of RS	Polymer structure	Relationship between the parameter of RS and structure parameters	Ref.
Largest Rouse relaxation time, λ_{rep}	linear chain in a tube	$\frac{3\xi N^3}{\pi^2 k}$	97
Relaxation time of the branch, λ_a	branched chain, stars	$\frac{\xi}{\pi^2 k}\exp\left(\frac{\nu N_a}{3}\right)$	97
Diffusion time of the centre of gravity, λ_D	dendrimer	$\frac{6g2^G\xi}{k}$	27
Relaxation time of the centre of gravity relative to the central atom, λ_s	"	$\frac{5\xi}{k}$	27
Relaxation time of rotational and internal elastic motion of monomeric units, $\lambda_r = \lambda_e$	"	$\frac{2^{g+1}\xi}{k}$	27

Note. ξ is the friction coefficient of a segment; N is the number of segments in the chain; $k = 3k_BT/a^2$, where k_B is the Boltzmann constant, T is the absolute temperature, a is the segment size; ν is the numerical coefficient the value of which depends on the model used;[154] N_a is the number of monomeric units in the branch.

As far as is known, only Gotlib and co-workers[28–30] have brought the theory to calculations of RS. In these studies, the dynamic model of dendrimers with an arbitrary functionality of branching points was considered, both external friction of branching points against environmental (ζ) and internal friction of points against each other (ζ_{int}) being taken into account. Two types of RS, internal and external, are distinguished. The internal relaxation spectrum corresponds to oscillating motion of branching points and takes the form

$$H_{int}(\lambda) = H_{int\,0}\left[4(f-1) - \left(\frac{1}{\lambda/\lambda_0 - p} - f\right)^2\right]^{-1/2} \frac{\lambda/\lambda_0}{(\lambda/\lambda_0 - p)^2},$$

where the relaxation time is expressed by the equation

$$\lambda = \zeta\left[Kf\left(1 - 2\frac{\sqrt{f-1}}{f}\cos\varphi\right)\right]^{-1} + \frac{\zeta_{int}}{K}$$

and is in the range between λ_{min} and λ_{max}:

$$\lambda_{min} = \zeta\left[Kf\left(1 + 2\frac{\sqrt{f-1}}{f}\right)\right]^{-1} + \frac{\zeta_{int}}{K},$$

$$\lambda_{max} = \zeta\left[Kf\left(1 - 2\frac{\sqrt{f-1}}{f}\right)\right]^{-1} + \frac{\zeta_{int}}{K}.$$

In these equations, f is the functionality of the branching point, $\lambda_0 = \zeta/K$, K is the modulus of elasticity of a coil spring that connects the branching points of the macromolecule; $p = \zeta_{int}/\zeta$; φ is the phase shift of vibration of the branching point, $\pi/g \leqslant \varphi \leqslant \pi(G-1)/G$.

The external spectrum reflects the pulsation motion of dendrimers or its parts relative to the centre and takes the form

$$H_{ext}(\lambda) = H_{ext\,0}(\lambda)\frac{\lambda/\lambda_0}{(\lambda/\lambda_0 - p)^2},$$

$$\lambda_j = \frac{\zeta(f-1)^{j+1}}{K(f-2)^2} + \frac{\zeta_{int}}{K},$$

$$\lambda_{min} = \frac{\zeta(f-1)^3}{K(f-2)^2} + \frac{\zeta_{int}}{K},$$

$$\lambda_{max} = \frac{\zeta(f-1)^{G+1}}{K(f-2)^2} + \frac{\zeta_{int}}{K},$$

j is the number of generation, $j = 2, \ldots, G$.

The exponential character of the time dependence of the relaxation modulus [see Eqn (4)] signifies that, as expected, RS of critical clusters is described by a power law (CW distribution),¶

$$H(\lambda) = H_0\left(\frac{\lambda}{\lambda_0}\right)^{-n}$$

for $\lambda_0 < \lambda < \lambda_{max}$, $0 < n < 1$, $\lambda_{max} \propto |\alpha_c - \alpha|^{-\gamma}$.

The time λ_0 determines the glass transition conditions and depends, like the front factor H_0, on the chemical structure of the polymer.

VI. Conclusion

From the aforesaid, unambiguous conclusions on the topological structures of HBP cannot be drawn. Actually, calculations with the use of data on the kinetics of formation[89, 271] provide evidence for MMD of polymers at nearly critical conversions but without consideration of the effects of cyclisation and exclusion volume. An approach based on the percolation model[59, 64] is suitable only for the critical conversion region and it is not quite clear whether it can be adequately applied to real systems and different degrees of conversion. Computer simulation accounts for the effects of cyclisation and exclusion volume,[53–55, 72, 74, 272] but it is difficult to relate these results to the real mechanism of formation of macromolecules. Apparently, this is why it is necessary to use the MMD model functions, for example, the Flory – Schultz distribution.[231]

The relaxation mechanisms of HBP are not associated with the presence of entanglements[59, 74] but are conditioned, like those of dendrimers, by intramolecular rearrangements. High elasticity is apparently attributed to interchain interactions between peripheral branches of highest-molecular-weight fractions.[20] However, it is apparently impossible to apply the theory of RS developed for dendrimers to HBP because it is necessary to take into account

¶ CW are the first letters of the last names of the authors of the studies.[222, 223]

irregularity of the architecture of HBP. To use CW spectra, one should first make sure that the topological structures of HBP are actually identical to those of critical clusters. Therefore, to get an insight into the relaxation mechanism of HBP, it is necessary, first, to refine understanding of their architecture and, second, develop a theory of relaxation spectra of HBP with a desired topological structure.

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