

## Hydrodynamic Characteristics of Branched Polystyrenes with Varying Content of a Highly Branched Fraction

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**Abstract**—The branched polymers containing different amounts of the highly branched fraction are synthesized by the radical copolymerization of styrene and divinylbenzene under conditions of the reversible inhibition by 2,2,6,6-tetramethylpiperidine-1-oxyl. The branched polystyrenes are studied by size-exclusion chromatography combined with static light scattering, viscometry, and pulsed-field gradient nuclear magnetic resonance. The branched polymers prepared by living radical polymerization (in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl) feature reduced intrinsic viscosities and increased self-diffusion coefficients compared with their linear analogs. As the content of the highly branched fraction in the synthesized polymers grows, the Zimm contraction factor in toluene solution decreases to  $g' = 0.13$ . The Kuhn–Mark–Houwink parameters for these polymers in toluene solution ( $a = 0.43$ ) confirm the nonlinear architecture of macromolecules.

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### INTRODUCTION

Highly branched polymers belong to the class of polymers which in terms of topology of macromolecular chains occupy the intermediate position between weakly branched polymers having single polymer chain branches and network polymers with a formally infinite number of branching points. Unfortunately, there is no generally accepted IUPAC terminology in this field [1] and many designations of the mentioned class of polymers are available in the literature. In our opinion, the term “highly branched” is the most universal because it is not related to the chemistry of macromolecule formation. In accordance with many authors, the term “hyperbranched” may be applied only to polymers formed by the polycondensation of the  $AB_n$  type monomers and thus distinguishes irregular branched polymers synthesized through one step [2–13] from dendrimers with the regular structure obtained via complex multistep synthesis [14–20]. According to this classification, branched polymers prepared by three-dimensional radical polymerization cannot be classified with hyperbranched polymers, although their topology and properties are similar. In the English literature, the term “random branched polymers,” which is also used for these polymers, suggests not so much topology as the method of forming branches; therefore, in our opinion, the term “highly branched polymers” is more preferable.

The presence of a large number of branching points at finite molecular masses provides the unique properties of highly branched polymers, namely, a low viscosity of solutions and melts and a high density of functional groups, which are of considerable interest in practice [21–23]. One of the methods for synthesizing highly branched polymers is three-dimensional radical polymerization, whose main advantage is the possibility to synthesize polymers from readily available and, therefore, rather cheap monomers, such as styrene and its derivatives, (meth)acrylates, etc. Highly branched polymers are synthesized by three-dimensional polymerization under conditions at which a network polymer that is formed under common conditions at monomer conversions  $<10\%$  [24] does not form at all or is formed at high conversions [25–45]. In the latter case, in order to synthesize soluble polymers, polymerization is stopped prior to the onset of gelation to give rise to the product containing both highly branched and linear and weakly branched macromolecules [30, 37, 38, 40, 46]. The latter no longer possess unique properties inherent in highly branched polymers and, hence, their presence should strongly affect the physicochemical properties of the product.

Our method of increasing the fraction of highly branched macromolecules in the polymeric product which is based on three-dimensional polymerization

conducted in the presence of a thermodynamically "poor" solvent makes it possible to synthesize branched polymers with different average numbers of branching points in macromolecules. Note that such parameters as the length of the primary polymer chain and the average distance between branching points remain invariable.

In this study, in order to gain insight into the effect of the average number of branching points in macromolecules on the hydrodynamic parameters of polymers, polystyrenes containing different amounts of the highly branched fraction synthesized by reversible deactivation three-dimensional polymerization were investigated by a combination of physicochemical methods.

## EXPERIMENTAL

### *Materials*

Styrene was treated with 10% NaOH aqueous solution to remove hydroquinone, washed with distilled water to a neutral reaction, dried over calcined  $\text{CaCl}_2$ , and distilled in vacuum. Technical divinylbenzene (Aldrich, 80 wt % DVB isomers) in ethylvinylbenzene (EVB) was used as received. Benzoyl peroxide and dicumyl peroxide (DCP) were recrystallized from ethanol solution, and 2,2,6,6-tetramethylpiperidine-1-oxyl was purified via sublimation. *n*-Butanol was dried over CaO and distilled in vacuum. Alkoxyamine was synthesized in situ at a temperature of 120°C by adding TEMPO and benzoyl peroxide at a molar ratio of 1.2 : 1.0 to the solution of monomers.

### *Synthesis of Branched Polystyrenes*

Branched polystyrenes were synthesized by the radical copolymerization of styrene and DVB in the absence and in the presence of *n*-butanol, which is a poor solvent for polystyrene at 120°C. Reversible deactivation polymerization was performed by adding TEMPO and benzoyl peroxide at a molar ratio of 1.2 : 1.0 to the solution of monomers in *n*-butanol. A high-temperature initiator DCP was also added to additionally increase the rate of polymerization. Before polymerization, reaction mixtures were outgassed via multiple freeze-pump-thaw cycles to a residual pressure of no more than 0.01 mmHg. Polymerization was conducted at 120°C in sealed ampoules and stopped before the onset of gelation (near the time of gelation). The resulting polymers were dried at room temperature under vacuum to remove *n*-butanol and unreacted monomers. The yield of the polymers was determined by thermogravimetry.

### *Analytical Methods*

The molecular-mass distribution of the polymers was analyzed by size-exclusion chromatography using

a Waters Alliance GPCV 2000 chromatograph (two PLgel 5- $\mu\text{m}$  MIXED-C columns connected in series, THF as an eluent, a flow rate of 1 mL/min,  $T = 35^\circ\text{C}$ ). The dried polymers were dissolved in THF, and the solution was filtered through an Anaton 25 0.2- $\mu\text{m}$  PTFE filter (Whatman). Chromatograms were registered using an RI differential refractometer at 900 nm and a MALLS DAWN HELEOS II Wyatt multiangle laser-light-scattering detector at 658 nm. The molecular mass of the polymers was measured by both the single-detector (SEC-DRI) technique using RI and calibration relative to polystyrene standards and the two-detector (SEC-DRI-MALLS) [47, 48] technique using RI to determine the concentration of eluted macromolecules and MALLS to estimate the absolute molecular mass of macromolecules at each time. Chromatograms were treated using Empower and ASTRA v. 5.3.2.20 software.

The intrinsic viscosity of highly branched polystyrenes in toluene solution at 19°C was determined by viscometry on a VPZh-2-type glass viscometer with a capillary diameter of 0.56 mm (LABTEX).

High-resolution NMR spectra were recorded on a Bruker Avance III spectrometer operating at a  $^1\text{H}$  NMR resonance frequency of 500.2 MHz. Self-diffusion studies were performed by stimulated echo pulsed field gradient NMR spectroscopy [49] on a Bruker Avance III spectrometer with a  $^1\text{H}$  NMR resonance frequency of 400.22 MHz. The spectrometer was equipped with a gradient system to obtain field gradient pulses with a maximum amplitude of 30 T/m.

## RESULTS AND DISCUSSION

### *Molecular-Mass Characteristics of Branched Polystyrenes with Different Content of the Highly Branched Fraction*

Table 1 shows the conditions of synthesis of the branched polymers. In the text that follows, the numbers of the synthesized polymers correspond to their numbers in the table. The regime of living chains was implemented via nitroxide-mediated polymerization, in which alkoxyamine was formed in situ from benzoyl peroxide and 2,2,6,6-tetramethylpiperidine-1-oxyl at the initial stages of the process. When the system was diluted with *n*-butanol, the rate of additional initiation controlled by the thermal self-initiation of styrene [50] decreased. As a result, the rate of the process declined, and at high dilutions, the process was fully suppressed. Therefore, a high-temperature initiator, dicumyl peroxide, was added to the system (the decomposition rate constant at 120°C is  $\sim 1 \times 10^{-5} \text{ s}^{-1}$  [51]) in an amount of 0.01 mol/L.

The molecular-mass characteristics of the polymers are listed in Table 2.

All of the polymers feature a high polydispersity index  $M_w/M_n$  due to the joining of primary polymer chains via the reaction of a radical of one growing

**Table 1.** Conditions of synthesis of branched polystyrenes ( $T = 120^\circ\text{C}$ )

Sample	Content of reagent, wt %						$t$ , min	$t_g$ , min	Yield, %
	styrene	DVB <sub>tech</sub>	<i>n</i> -butanol	TEMPO*	benzoyl peroxide*	DCP**			
1	98.14	1.86	0	0.86	1.11	0.30	300	355	65.4
2	70.45	1.34	28.21	0.86	1.11	0.30	500	550	64.7
3	50.86	0.96	48.18	0.86	1.11	0.30	480	600	75.4
4	50.86	0.96	48.18	0.86	1.11	0.30	530	600	77.3

$t_g$  is the time of gelation.

\*Content with respect to monomers.

\*\*Content with respect to the whole solution.

**Table 2.** Molecular-mass characteristics of branched polystyrenes determined by one-detector (SEC-DRI) and two-detector (SEC-DRI-MALLS) techniques

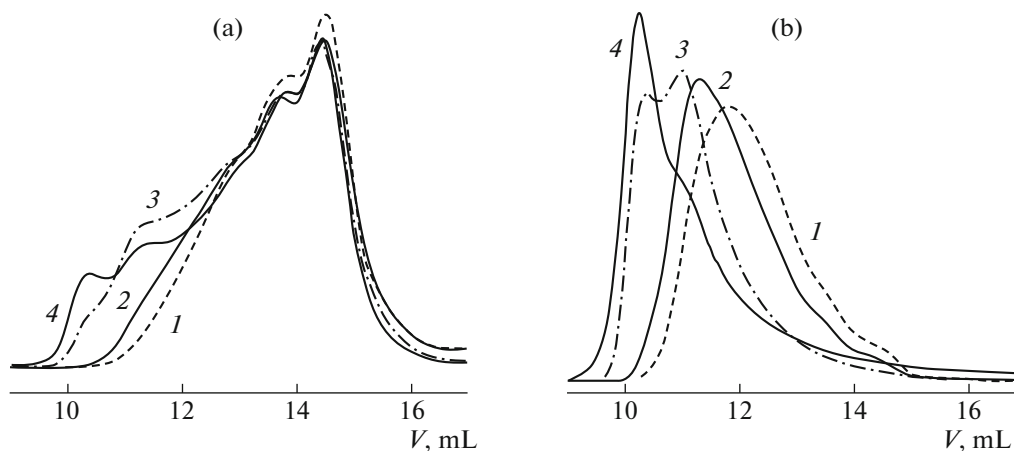
Sample	SEC-DRI			SEC-DRI-MALLS		
	$M_n$	$M_w$	$M_w/M_n$	$M_n$	$M_w$	$M_w/M_n$
1	17800	72000	4.0	25000	132000	5.3
2	19400	101000	5.2	31000	201000	6.5
3	20700	197000	9.5	64000	568000	8.9
4	18000	236000	13.1	409000	1600000	3.9

chain with the pendant double bond of another primary chain. For such systems, a high polydispersity index usually indicates formation of polymers containing highly branched macromolecules composed of several primary polymer chains.

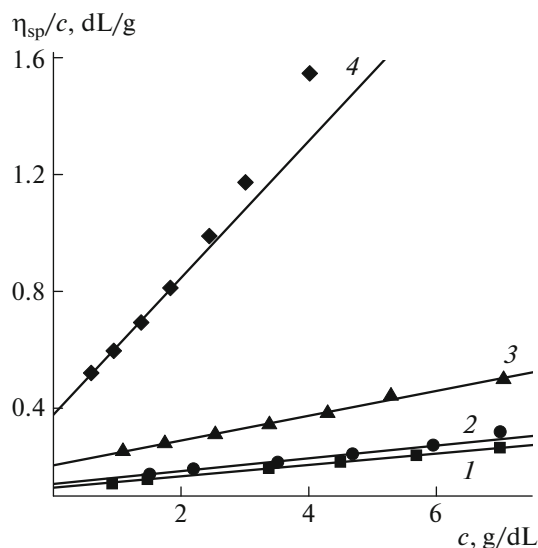
Noteworthy is an important feature: the main peak on the chromatographic curves (Fig. 1a) associated with the primary polymer chains occurs in the same elution volume range. The molecular mass corresponding to this peak for all of the polymers is  $(1.4$ –

$1.5) \times 10^4$ , in good agreement with the initial conditions of synthesis that should provide a molecular mass of primary polymer chains of  $\sim 1.8 \times 10^4$  upon full consumption of the monomer. Hence, branched macromolecules are composed of primary polymer chains with a molecular mass of  $(1.4$ – $1.5) \times 10^4$ .

A marked shift of the chromatographic curves registered by the multiangle laser-light-scattering detector (Fig. 1b) to smaller elution times provides addi-



**Fig. 1.** Chromatograms of branched polystyrenes (1) 1, (2) 2, (3) 3, and (4) 4 registered by (a) the refractometric detector and (b) the multiangle laser-light-scattering detector at an angle of  $90^\circ$ . The areas under the chromatographic curves are reduced to the corresponding yields in Table 1 or to unity (b).



**Fig. 2.** Dependence of reduced viscosity on the concentration of toluene solutions of branched polystyrenes 1 (1), 2 (2), 3 (3), and 4 (4).  $T = 19^\circ\text{C}$ .

tional evidence that highly branched macromolecules are contained in the polymeric product.

In order to estimate the content of highly branched macromolecules, to which macromolecules composed of no less than seven primary polymer chains are assigned [46] (for these macromolecules, the Zimm factor  $g$  is less than 0.5 [52]), in the polymeric product, areas under the left branch of chromatographic curves intercepted by the vertical line at an elution volume of 13.12 mL were calculated. This corresponds to a molecular mass of  $9 \times 10^4$  in accordance with the single-detector technique. The mass fraction of highly branched macromolecules in polymers 1, 2, 3, and 4, which was estimated as described in [53], is 0.28, 0.34, 0.42, and 0.41, respectively. Note that for polystyrenes 3 and 4, the mass fraction of highly branched macromolecules is the same; however, for the latter polymer, the molecular-mass distribution in the region of highly branched macromolecules is shifted to the macromolecules with a higher molecular mass and,

**Table 3.** Hydrodynamic parameters of branched polystyrenes with different content of the highly branched fraction in strongly dilute toluene solutions ( $T = 19^\circ\text{C}$ )

Sample no.	$[\eta]_0$ , dL/g	$k_h$	$g'$
1	0.129	1.17	0.31
2	0.141	1.09	0.24
3	0.205	1.08	0.16
4	0.378	1.64	0.13

accordingly, with a larger number of branching points. Exactly this fact explains a higher weight-average molecular mass of branched polystyrene 4 (Table 2).

#### *Hydrodynamic Parameters of Branched Polystyrenes with Different Amount of the Highly Branched Fraction*

An important characteristic of branched polymers is hydrodynamic parameters of their dilute solutions. Figure 2 shows the dependence of reduced viscosity on polymer concentration. The experimental curves are rectified in the coordinates of the equation

$$\frac{\eta_{sp}}{c} = [\eta]_0 + k_H[\eta]_0^2 c,$$

where  $[\eta]_0$  is the intrinsic viscosity of the polymer in a given solvent at a given temperature and  $k_H$  is the Huggins constant.

The values of intrinsic viscosity and the Huggins constant of the branched polystyrenes in toluene at  $19^\circ\text{C}$  are listed in Table 3. The average number of branching points in macromolecules is estimated using the so-called Zimm contraction factor:

$$g' = \frac{[\eta]_{obr}}{[\eta]_{olin}},$$

where  $[\eta]_{obr}$  and  $[\eta]_{olin}$  are the intrinsic viscosities of branched and linear polymers of the same molecular mass.

The values of  $[\eta]_{olin}$  were calculated according to the Kuhn–Mark–Houwink equation:

$$[\eta]_0 = K_w \times M_w^a.$$

The intrinsic viscosity of the linear analog of the branched polystyrenes was derived from its number-average molecular mass  $M_w$ , which was determined by the two-detector technique (SEC-DRI-MALLS). Calculation was performed taking into account correction for polydispersity of the polymer  $K_w = 0.935 \times K$  [52], where  $K$  is a constant, which for polystyrene in toluene at  $20^\circ\text{C}$  is  $4.16 \times 10^{-5}$  (dL/g) [54], at parameter  $a = 0.788$ . According to light-scattering studies [54], the molecular mass of linear polystyrene is  $4 \times 10^4 - 1.37 \times 10^6$ . Because the synthesized polymers are nonuniform in terms of the architecture of macromolecules (they contain linear and weakly and highly branched macromolecules), only the apparent Zimm contraction factor may be estimated. The value of this factor makes it possible to compare polymers and to qualitatively estimate the effect of the number of branching points in macromolecules on the degree of compression of a macromolecular coil. As follows from Table 3, the apparent Zimm contraction factor for the polymers of interest decreases with an increase in the share of *n*-butanol in the system and on approach to the gel point. These results evidently suggest that the average number of branching points increases in the sequences of samples  $1 < 2 < 3 < 4$ . An

increase in the number of branching points in the sequence of the studied polymers is explained by an increase in the fraction of highly branched macromolecules composed of a greater number of primary polymer chains and, therefore, having a higher molecular mass, as is clearly reflected by the molecular-mass characteristics of the polymers.

All of the studied polymers have primary polymer chains with approximately equal lengths, because radical polymerization is conducted in the regime of living chains, therefore the average length of a chain between branching points and between the end branching point and the end of a primary polymer chain should be the same for all of the polymers. In fact, the polymers under consideration differ only in the width of molecular-mass distribution and in the average number of branching points in a macromolecule; that is, they are topological homologs. If linear polymer homologs differ in the number of monomer units in a chain, then, in the case of branched polymers synthesized by living three-dimensional radical polymerization, topological homologs differ in the number of primary polymer chains having equal lengths. Here we may draw analogy to the topological homologs of star-shaped polymers, for which the number of these homologs grows with the length of polymer arms being invariable. This also leads to reduction in the Zimm factor [52].

Noteworthy is a high value of the Huggins constant  $k_H$ , which is above unity and attains 1.64. For the sake of comparison, for linear polystyrenes in toluene at 21°C,  $k_H$  is in the range of 0.25–0.35 [54]. High values of the Huggins constant provide evidence for the compact state of macromolecules in solution. This indicates that highly branched macromolecules are contained in the polymers, because the compactness of macromolecules is provided by the restricted freedom of displacement of its fragments owing to the presence of branching points in them.

Proceeding from the intrinsic viscosity and weight-average molecular mass of the polymers, the Kuhn–Mark–Houwink constants were estimated (Fig. 3). For toluene at 19°C they are  $K = 74.1 \times 10^{-5}$  dL/g and  $a = 0.43 \pm 0.05$ . Note that constant  $a$ , which is defined by the asymmetry of a macromolecule in solution, is much lower compared with linear polystyrenes in the same solvents and is much smaller than a value of 0.5 typical for  $\theta$  conditions. Thus, all of the above-described data unambiguously confirm the nonlinear architecture of the synthesized macromolecules.

It should be mentioned once again that all of the studied polymers feature a wide molecular-mass distribution; therefore, the values of the Zimm factor, Huggins constant, and Kuhn–Mark–Houwink parameters should be regarded only as estimates that need correction. For this purpose, polymers with a narrow molecular-mass distribution, that is, polymer fractions, should be studied. At the same time, we

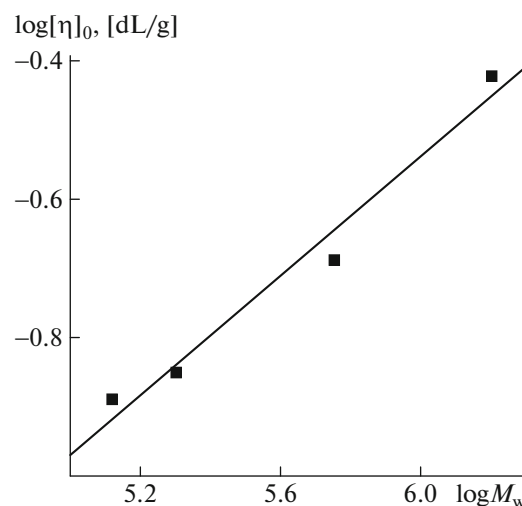


Fig. 3. Dependence of the intrinsic viscosity of the synthesized polymers in toluene at 19°C on their molecular mass in logarithmic coordinates.

believe that, for branched polymers synthesized by living three-dimensional radical polymerization, determination of the Kuhn–Mark–Houwink parameters is possible only in the case of topological homologs, for which an increase in molecular mass is associated with an increase in the number of branching points with the distance between them being constant. Otherwise, when an increase in molecular mass is related to an increase in the distance between branching points with their number being constant, the slope of dependences in Kuhn–Mark–Houwink coordinates will grow, because with increasing molecular mass the ratio between the number of branching points and the total number of monomer units in a macromolecule will decrease and the exponent in the Kuhn–Mark–Houwink equation will approach the value typical for linear polymers.

#### *Translational Mobility of Macromolecules of Branched Polystyrenes with Different Amount of the Highly Branched Fraction*

The study of the translational mobility of macromolecules provides a way to obtain valuable information about their dimensions, shape, and flexibility. If the viscosity of polymer solutions describes the macroscopic transfer of a substance related to the collective motion, self-diffusion is associated with the displacement of individual molecules related to their thermal motion. Pulsed magnetic field gradient NMR spectroscopy is in wide use for the study of self-diffusion.

The self-diffusion coefficients of the branched polystyrenes in protonated toluene solutions were measured by the stimulated echo pulsed field gradient NMR method [55]. Self-diffusion coefficients  $D$  in

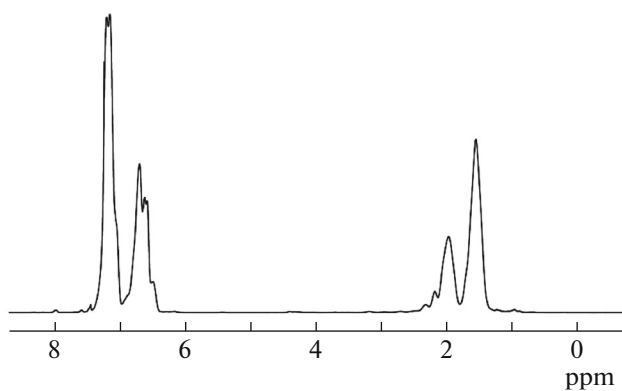


Fig. 4.  $^1\text{H}$  NMR spectrum of branched polystyrene solution in  $\text{CDCl}_3$ .

the pulsed field gradient NMR spectroscopy are determined from the dependence of intensity of echo signal on magnetic field gradient, which is called the diffusion decay:

$$A(g) = A(0) \exp(-\gamma^2 g^2 \delta^2 D t_d), \quad (1)$$

where  $A(0)$  is the amplitude of echo in the absence of field gradient;  $\gamma$  is the gyromagnetic ratio of a nucleus;  $g$  and  $\delta$  are the amplitude and time of gradient pulse, respectively;  $t_d = \Delta - \delta/3$  is the effective time of diffusion observation; and  $\Delta$  is the time interval between gradient pulses.

During determination of self-diffusion coefficients, the amplitude of gradient field pulses was changed (at fixed  $\delta = 1$  ms and  $t_d = 30$  ms). For polymers, the diffusion decay is a sum of contributions from macromolecules with different self-diffusion coefficients:

$$A(g) = A(0) \sum_i p_i \exp(-\gamma^2 g^2 \delta^2 D_i t_d), \quad (2)$$

where  $p_i$  is the fraction of macromolecules with the self-diffusion coefficient  $D_i$  and  $\sum_i p_i = 1$ .

The expansion of Eq. (2) in a Taylor series at small gradient amplitudes  $g$  makes it possible to obtain the value of the self-diffusion coefficient averaged over all macromolecules  $\bar{D} = \sum_i p_i D_i$  as a slope of the diffusion decay curve at  $g^2 \rightarrow 0$ :

$$A(g) = A(0) (1 - \gamma^2 g^2 \delta^2 t_d \bar{D}). \quad (3)$$

The typical spectrum of branched polystyrene solution in deuterated chloroform is presented in Fig. 4. The spectrum consists of four characteristic regions: signals at 1.6 ppm are due to protons of  $\text{CH}_2$  groups, signals at 2 ppm are due to protons of  $\text{CH}$  groups, and signals at 6.7 and 7.2 ppm are due to aromatic protons.

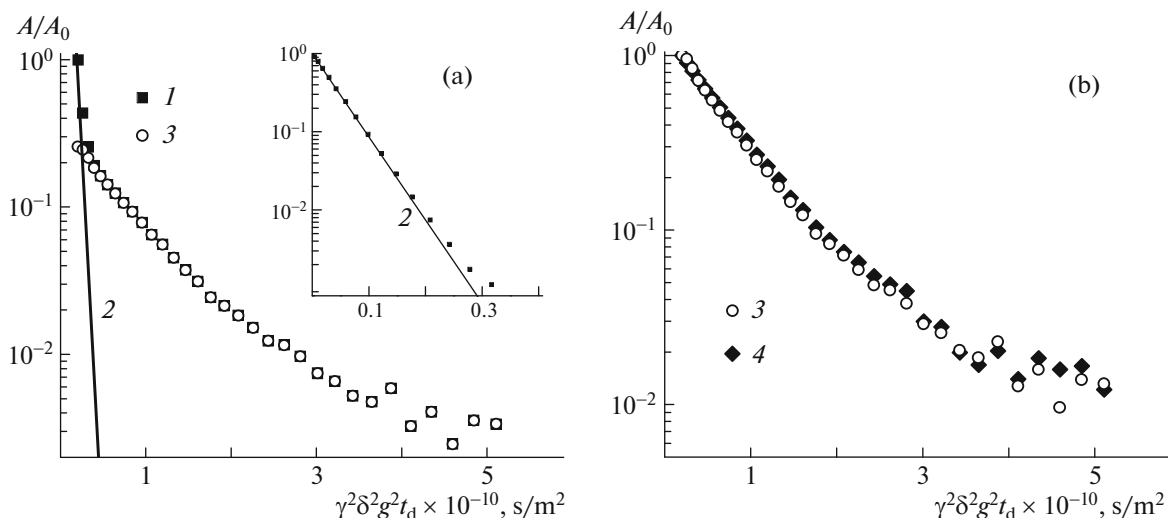
In order to compare the Kuhn–Mark–Houwink parameters found for the toluene solutions of

branched polystyrenes, self-diffusion was also studied by pulsed field gradient NMR spectroscopy in toluene solution. The self-diffusion coefficients of individual solution components were determined using the Fourier transform of spin-echo signals. The value of  $A(g)$  at various gradient amplitudes  $g$  was estimated from the integral intensity of the line in the spectra.

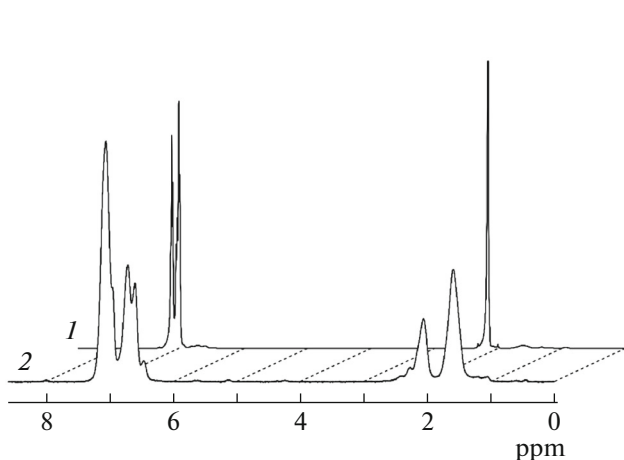
The typical diffusion decay curve for solutions of branched polystyrenes in toluene which was obtained by the integration of signals in the range of 1–3 ppm is shown in Fig. 5a (curve 1). Two regions may be distinguished on this curve. The initial region is primarily determined by the decay of toluene signals. At small amplitudes of gradient pulses ( $\gamma^2 g^2 \delta^2 t_d < 0.2 \times 10^{10}$  s/m<sup>2</sup>), the observed stimulated echo spectrum is a spectrum typical for the protons of toluene (Fig. 6, spectrum 1). The final region is defined by the decay of polymer signals; at large amplitudes ( $\gamma^2 g^2 \delta^2 t_d > 1.5 \times 10^{10}$  s/m<sup>2</sup>), the spectrum is typical of polystyrene (Fig. 6, spectrum 2).

This difference in self-diffusion coefficients allows the diffusion decay to be estimated for toluene at  $\gamma^2 g^2 \delta^2 t_d < 0.2 \times 10^{10}$  s/m<sup>2</sup> in a separate experiment, where the initial region is studied with a small step of change in gradient  $g^2$  (Fig. 5a, inset), and then to be extrapolated to high gradient values (Fig. 5a, curve 2). Subtraction of the diffusion decay of toluene from the  $A(g)$  of the polymer solution (Fig. 5a, curve 1) yields the diffusion decay separately for branched polystyrenes (Figs. 5a, 5b, curve 3). The validity of this approach was verified using solutions with a high concentration of the polymer ( $\sim 5$  g/dL), where the self-diffusion coefficient of polystyrene may be selectively measured from the signal of the  $\text{CH}_2$  group (1.6 ppm). Figure 5b shows the diffusion decay curves of polystyrene which were obtained from the signals of  $\text{CH}_2$  groups (curve 4) not overlapping with the signals of toluene and subtraction of the decay of toluene from the total decay (curve 3). It is seen that the diffusion decay curves of polystyrene determined by different methods are in good agreement; therefore, in further experiments performed at low concentrations of polystyrene in toluene, the subtraction-based method was used.

Figure 7 shows the diffusion decay curves of the branched polystyrenes in toluene solutions at concentrations of  $\sim 1$  g/dL. For all of the samples, the decay deviates from the exponential pattern because of the presence of a wide molecular-mass distribution. The most pronounced deviation is observed for polystyrene 4 with the widest molecular-mass distribution (Table 2). Average self-diffusion coefficients were calculated from the initial slope of the diffusion decay curve using Eq. (3).



**Fig. 5.** (a) Diffusion decay curves of (1) toluene–polystyrene system, (2) toluene, and (3) polystyrene; (b) renormalized diffusion decay of polystyrene obtained (3) by subtraction and (4) from the signals of CH<sub>2</sub> groups.



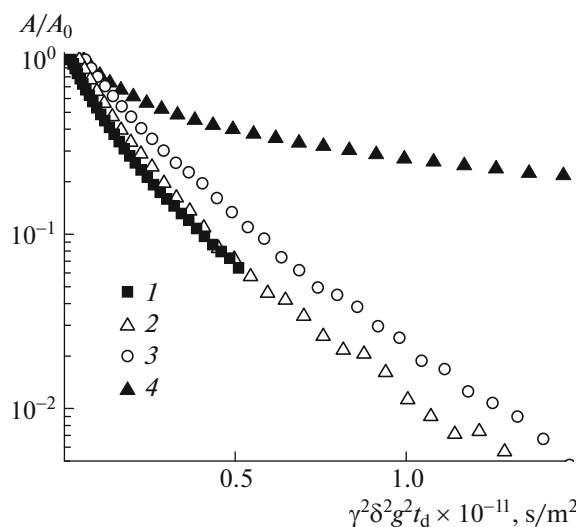
**Fig. 6.** Stimulated-echo <sup>1</sup>H NMR spectra registered at small (1) (the initial portion of diffusion decay) and large (2) amplitudes of gradient pulses (the scale of the spectrum is increased for clarity).

The concentration dependence of the average self-diffusion coefficient of the polymer may be described by the function [55]

$$\bar{D} = D_0 \exp(-kc),$$

where  $c$  is the concentration,  $D_0$  is the self-diffusion coefficient of the polymer in the ultimately dilute solution, and  $k$  is a constant depending on the properties of a solvent and polymer.

Figure 8 presents the concentration dependences of self-diffusion coefficients. It should be noted that, in the studied concentration range with an increase in concentration, the measured self-diffusion coefficients of toluene ( $2.4 \times 10^{-9}$  m<sup>2</sup>/s) decrease insignifi-



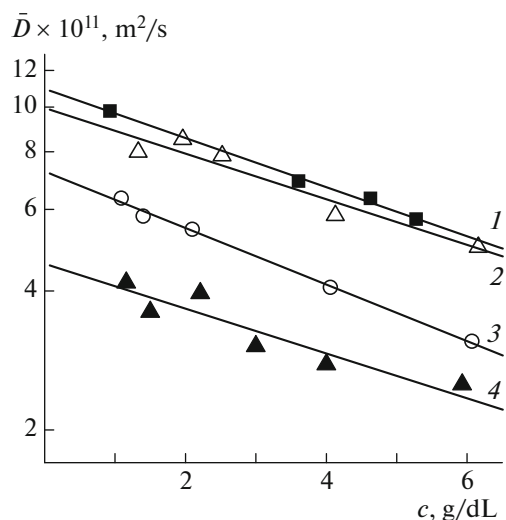
**Fig. 7.** Diffusion decay curves for samples of branched polystyrenes (1) 1, (2) 2, (3) 3, and (4) 4 at a concentration of ~1 g/dL.

cantly (by less than 10%). This value is only slightly above the measurement error, whereas the self-diffusion coefficients of the polymers change by a factor of nearly 2.

Table 4 summarizes the values of  $k$  and  $D_0$  for polystyrenes in the ultimately dilute solution. These data were used to calculate the values of hydrodynamic radius:

$$R_H = \frac{k_B T}{6\pi\eta D_0},$$

where  $\eta$  is the viscosity of a pure solvent at a given temperature and  $k_B$  is the Boltzmann constant.

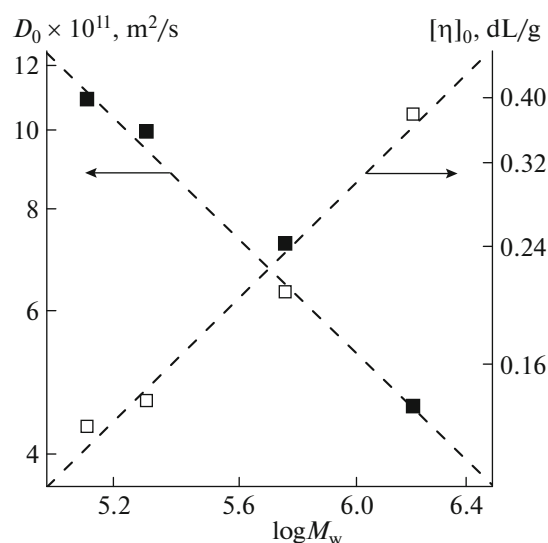


**Fig. 8.** Dependence of self-diffusion coefficient of polystyrenes (1) 1, (2) 2, (3) 3, and (4) 4 on concentration in dilute toluene solutions at 23°C.

Using a simple phenomenological model [55–58], in accordance with which individual macromolecules freely diffuse in a solvent and do not experience the hydrodynamic effect of other macromolecules except rare collisions, while macromolecules being in contact diffuse as a whole for a certain time and then again become independent, then for the self-diffusion coefficient of macromolecules in dilute solutions we may write  $D(c) = D_0 \exp(K_z V_m c)$ , where  $c$  is the concentration,  $V_m$  is the volume of a macromolecule in solution, and  $K_z$  is the parameter of interaction between polymer coils. In the series of studied polystyrenes, the volume of a macromolecule  $V_m$  grows simultaneously with the number of branching points in a macromolecule, so that its molecular mass is directly proportional to the amount and molecular mass of primary polymer chains. Because the slope  $k = K_z V_m$  for straight lines in Fig. 8 changes insignificantly, it may be assumed that parameter  $K_z$  decreases. Weakening of interaction between polymer coils may be explained by reduction in the probability of entanglement of macromolecules. This parameter is connected with the degree of swell-

**Table 4.** Hydrodynamic parameters of dilute solutions of the branched polystyrenes

Sample no.	$D_0 \times 10^{11}, \text{m}^2/\text{s}$	$k, \text{dL/g}$	$R_H, \text{nm}$
1	10.94	0.12	3.3
2	9.95	0.11	3.7
3	7.25	0.14	5.0
4	4.58	0.11	8.0



**Fig. 9.** Dependence of self-diffusion coefficient  $D_0$  and intrinsic viscosity  $[\eta]_0$  of branched polystyrenes in toluene solution on their molecular mass.

ing of a macromolecular coil, which decreases with increasing number of branching points.

#### *Kuhn–Mark–Houwink Parameters for Toluene Solutions of Branched Polystyrenes*

The dependence of the self-diffusion coefficient on molecular mass is described by the well-known expression

$$D_0 = K_b \times M_w^{-b}$$

In Fig. 9, the dependence of self-diffusion coefficients of the branched polystyrenes in toluene on their molecular mass is plotted for the sake of comparison together with the corresponding dependence of intrinsic viscosity.

The experimental coefficient  $b$  ( $0.35 \pm 0.03$ ) is much smaller than the value of 0.5 typical for linear polymers under  $\theta$  conditions. These low values of exponents are typical for branched macromolecules and dendrimers in good solvents [59–61]. For linear polystyrenes in toluene solution at 20°C,  $b = 0.574$ , as estimated by dynamic light scattering [62].

Exponent  $a = 0.43 \pm 0.05$  is much lower than that for linear flexible-chain polymers ( $a = 0.6–0.8$ ) and is higher than the values typical for dendrimers ( $a = 0–0.2$ ) [61]. These data suggest the presence of highly branched macromolecules in the synthesized polystyrenes.

It should be noted that constants  $a$  and  $b$  were estimated from the dependence of the hydrodynamic parameters of polymers on their weight-average molecular mass. As is known from the study of polydisperse linear flexible-chain polymers, the viscometrically measured parameter  $a$  is sensitive to the



content of the high-molecular-mass component and correlates well with the value of  $M_w$ . In accordance with [55], parameter  $b$ , which was calculated from the pulsed-field gradient NMR data, better correlates with  $M_n$ . The presence of linear and weakly branched chains in the synthesized polystyrenes will cause an increase in both parameters. For a more correct determination of parameters  $a$  and  $b$ , fractions of highly branched polystyrenes free of linear and weakly branched macromolecules should be examined.

The Kuhn–Mark–Houwink parameters  $a$  and  $b$  depend on the solvent quality and in the general case may be written as follows [63]:

$$a = a_\theta + 3\varepsilon$$

$$b = b_\theta + \varepsilon,$$

where  $a_\theta$  and  $b_\theta$  are the Kuhn–Mark–Houwink parameters for  $\theta$  conditions and  $\varepsilon$  is the parameter allowing for polymer–solvent interaction.

In good solvents condition  $a > b$  is always fulfilled, and only under  $\theta$  conditions do they become equal. For linear polymers under  $\theta$  conditions,  $a_\theta = b_\theta = 0.5$ . For the synthesized branched polystyrenes, condition  $a > b$  is also fulfilled, and from equality  $a - b = 2\varepsilon$ , we may find parameter  $\varepsilon = 0.04 \pm 0.03$ . Hence, for the branched polystyrenes, we obtain  $a_\theta = 0.31 \pm 0.10$  and  $b_\theta = 0.31 \pm 0.04$ . The calculated parameter  $b_\theta$  ( $0.31 \pm 0.04$ ) is close to the minimal theoretical value of  $b = 1/3$ , to which constant  $a = 0$  corresponds. At the same time,  $a_\theta = 0.31 \pm 0.10$ ; hence, the theoretical equation  $b = (a + 1)/3$  is not fulfilled [63]. This is apparently associated with the experimental error, because constants  $a$  and  $b$  are determined for the samples with a wide molecular-mass distribution. In addition, the studied polymers are topological homologs, for which the above-mentioned equality may be invalid.

Thus,  $\theta$  conditions for the branched polymers may differ appreciably from  $\theta$  conditions for the linear polymer with the analogous chemical nature. Under  $\theta$  conditions typical for the linear polymer, the macromolecule of the branched polymer occurs in the swollen state because steric hindrances occurring in the vicinity of branching points hamper its folding. To overcome these limitations, the thermodynamic quality of the solvent should be worsened to the level where the repulsion of chain segments in the vicinity of branching points will be compensated by the additional attraction of chains [64].

Note that, with consideration of these ideas about the behavior of branched polymers in strongly dilute solutions, our method of determining parameters  $a_\theta$  and  $b_\theta$  provides a way to compare branched polymers with different chemical nature, topology (functionality of branching points, etc.), and degree of branching. Polymers with the highest degree of branching should be characterized by the lowest values of parameters  $a_\theta$  and  $b_\theta$ . A comparison of branched polymers in terms

of the values of  $a_\theta$  and  $b_\theta$ , as opposed to comparison in terms of the degree of branching  $DB$ , which is usually calculated from the high-resolution NMR data, takes into account the physical behavior of macromolecules in solution. This comparison makes it possible to arrive at more careful conclusions about advantages and disadvantages of various methods used to prepare branched polymers and the effect of chain architecture on their macroscopic properties. However, the validity of the developed approach requires verification for a wide scope of objects.

## CONCLUSIONS

Branched and highly branched polystyrenes have been synthesized by the living three-dimensional radical polymerization (the alkoxyamine variant) in the absence and in the presence of *n*-butanol as a precipitator of polystyrene chains. It has been shown that the presence of the precipitator ensures an increase in the polydispersity index of the resulting polymers owing to accumulation of highly branched macromolecules in the system.

It has been found that the branched polymers with the increased content of highly branched macromolecules have much underestimated values of the Zimm contraction factor and Kuhn–Mark–Houwink constants  $a$  and  $b$  characterizing the asymmetry of macromolecules in solution and higher self-diffusion coefficients compared with the linear analogs of the same molecular mass.

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