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Self-Diffusion and Nuclear Magnetic Relaxation of Dendritic Macromolecules in Solutions

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Abstract. The self-diffusion and nuclear magnetic relaxation of poly(butylcarbosilane) and poly(allylcarbosilane) dendrimers dissolved in deuterated chloroform and poly(amidoamine) dendrimers with hydroxyl surface groups in solutions with methanol have been studied. The diffusion rates (D) have been measured by the pulsed-field-gradient nuclear magnetic resonance. It is shown that experimental concentration dependences $D(\varphi)$ obtained for macromolecules in the dendrimer-solvent systems studied can be reduced to a unified view, and thus, the generalized concentration dependence of the normalized diffusion rates of dendrimers can be obtained. In the macromolecular volume concentration range from 0.01 up to 0.55, the generalized dependence of the normalized diffusion rates for dendrimers coincides with the analogous dependence for globular proteins in aqueous solutions; the last result suggests that self-diffusion features of dendrimers and globular proteins are in general similar. It is also shown that the experimental data obtained permit one to characterize the changes of the own monomer density of dendrimers depending on their molecular weight and, as a consequence, to make a conclusion about the swelling of dendritic macromolecules in the solutions studied.

1 Introduction

The development of modern technologies essentially depends on progress in production of novel materials including the synthetic oligo- and polymers with specified chemical and physical properties. As a result of investigations and work in the field of supramolecular chemistry [1–6], developing since the second half of 1970s, new types of macromolecules have been obtained [5–10].

1.1 Dendrimers: General Notions

The cascade superbranched polymers, dendrimers [4, 6], are a unique class of supramolecular compounds obtained in the course of a controlled stepwise syn-

thesis. The planar sketch of a dendritic macromolecule composed of equal-length segments is depicted in Fig. 1. In accord with the name of these polymers ("dendrimer"; in Greek, dendron means branch, tree), the dendrimer interior chains are called the crown (or cell), where the core, repeat units and terminal groups are distinguished (see Fig. 1). Each unit in general determines the main characteristics of macromolecules: their size, topology, chain flexibility, chemical functionality, maximal molecular weight reachable in the case of a dendrimer ideally growing [4–10].

Recently, a number of effective strategies of the dendrimer synthesis have been developed and published in a series of reviews [4, 6–8]. Taking into account the main results of these works it should be admitted that dendrimers are undoubtedly of interest to study their chemical-physical properties in order to determine the areas of their practical applications (for instance, for production of nanoobjects, for preparing high-performance catalysts and novel medical drags).

Inasmuch as all common stages of the synthesis of dendrimers and compounds obtained on their basis are conducted in the solutions of initial components, the information about translational mobility of dendrimers in solutions seems to be a topical problem. Most of modern results concerning properties of dendrimers in solutions mainly characterize the structural features of macromolecules and supermolecular structure of such solutions [18–25]. The experimental data describing the features of the dendrimer translational mobility in the dendrimer-solvent systems are reported in a few works [26–28]. The aims were mainly to determine the hydrodynamic radii of dendrimers through macromolecular diffusion rates (D) and the Stokes-Einstein formula [27] and to elucidate how the macromolecular size changes depending on the solvent [26, 27]. The measurements of dendrimer D were performed by the pulsed magnetic field-gradient nuclear magnetic resonance (PFG NMR) with relatively low values of the PFG amplitude g_{max} (up to 0.53 T/m). Moreover, the effects of the macromolecular concentration on the dendrimer mobility were not studied in these works [26, 27].

The most thorough and detailed study of the diffusion behavior was reported by Rietveld et al. [28] for the dendrimer solutions. As follows from ref. 28, for solutions of the first-, second- and third-generation poly(propylene imine) den-

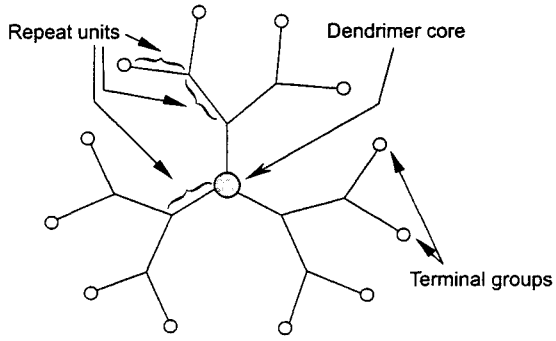

Fig. 1. Molecular structure of a dendrimer.

drimers over the whole range of the macromolecular volume concentrations examined ($0 < \varphi \leq 1$) and for macromolecules of the fourth and fifth generations over the concentration range from 0 up to 0.4, the dependence $D(\varphi)$ is satisfactorily described within the frames of the free-volume theory developed by Vrentas and Duda [23–25, 29]. However, it was impossible to describe the dependence $D(\varphi)$ obtained for macromolecules of the fourth and fifth generations in this simple approach for the macromolecular volume concentrations $\varphi > 0.4$. This result allowed the authors to relate this concentration range to the regime of concentrated solutions. For poly(propylene imine) dendrimers of the three lowest generations the regime of concentrated solutions was not found.

It should be noted that in refs. 26–28 the self-diffusion of only low- and middle-generation (usually, $G = 4$–5) dendrimers was studied. The diffusion behavior of high-generation ($G > 5$) macromolecules remained unexamined, although some physical properties of low- and high-generation dendrimers differ considerable [4, 6, 7]. Only Rietveld et al. [28] reported a study of the macromolecular self-diffusion over a wide enough dendrimer concentration range. Nevertheless, it was not possible to explain the character of concentration dependences $D(\varphi)$ obtained for poly(propylene imine) dendrimers of the fourth and fifth generations within the frames of a general approach over the whole concentration range studied.

Thus, the amount of experimental material concerning the transport properties of dendrimers of various generations in real solutions and blends remains insufficient at present, and perhaps as a consequence, general theory which would describe the dynamic properties of dendritic macromolecules is still not developed.

1.2 NMR Diffusometry: Technique of Stimulated Spin-Echo with Pulsed Gradient of Magnetic Field

The PFG NMR is considered as an effective technique to study the molecular translational mobility in condensed matter [29, 30, 34–36]. One can determine the values of diffusion rates D of molecules and macromolecules by detecting the spin-echo signal changes due to the distribution of spatial displacements of the resonant nuclei in a magnetic field with a gradient and nuclear magnetic relaxation processes. The technique of stimulated spin-echo (see Fig. 2) with a pulsed-field gradient developed and proposed by Stejskal and Tanner [37] gives much information about the molecular self-diffusion. If the condition $g\delta \gg g_0\tau$ holds (here g and δ are the amplitude and duration of PFG, respectively, g_0 is the steady gradient of the magnetic field, τ is the delay between the first and second 90° radio-frequency (rf) pulses in the given sequence), then the amplitude of the spin-echo signal is described by the relation [30, 37]

$$\frac{A(2\tau,\tau_1,g)}{A(2\tau,\tau_1,0)} \equiv \frac{A(\gamma^2 g^2 \delta^2 t_d)}{A(0)} = \sum_i p_i' \exp(-\gamma^2 g^2 \delta^2 D_i t_d), \quad (1)$$

where the apparent population

$$p_i' = \frac{p_i \exp(-2\tau/T_{2i} - \tau_1/T_{1i})}{\sum_i p_i \exp(-2\tau/T_{2i} - \tau_1/T_{1i})},$$

p_i is the true population of the i-th component, τ_1 is the time delay between the second and third 90° rf pulses, γ is the gyromagnetic ratio of resonant nuclei, $A(0) = A(2\tau, \tau_1, 0)$ is the amplitude of the stimulated spin-echo at $g = 0$, D_i, T_{1i} and T_{2i} are the diffusion rate, the spin-lattice and spin-spin nuclear magnetic relaxation times for the i-th component of system studied, respectively. Equation (1) is conventionally called the diffusion decay (DD) of the spin-echo amplitude. The values D_i and p_i of the corresponding components of the system studied are obtained from the analysis of the DD shape [29, 30, 34].

The use of a relatively high value of PFG (for instance, g_{max} = 30–50 T/m) permits one to measure the diffusion rates of the order of 10^{-13}–10^{-15} m²/s [38–43] characteristic, in particular, for polymers with molecular weights high enough in concentrated solutions and melts.

The aim of this work is to study the macromolecular self-diffusion in solutions of symmetrical dendrimers differing by their chemical nature, structure (i.e., different families) and generations (including high-generation dendrimers) over the wide enough polymer concentration range by PFG NMR. In spite of its specific topology, a dendrimer represents a macromolecule composed, similar to the typical polymeric chains, of the monomeric units: repeat units and

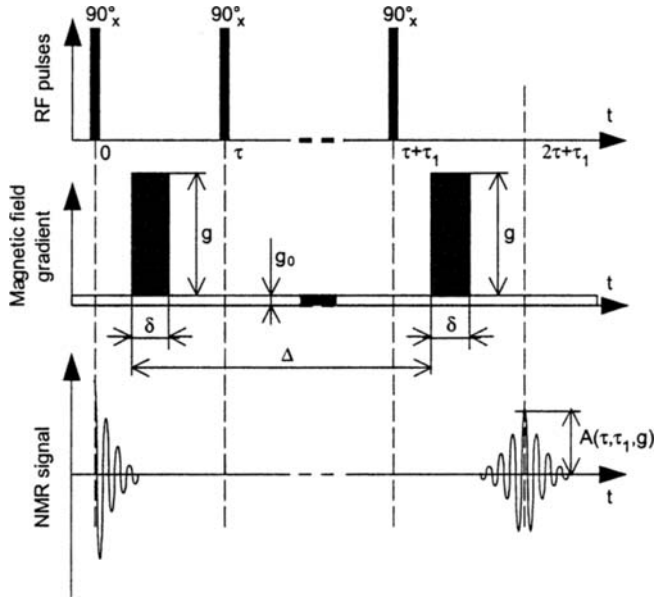

Fig. 2. Pulse sequence of the stimulated spin-echo [37].

terminal groups. On the basis of this fact, the analysis of experimental data has been made within the frames of basic aspects of de Gennes theory of dynamic scaling [44] and approaches [29, 40, 42] developed by the examples of analyzing the concentration and molecular-mass (M) dependences of D for various linear polymers.

2 Materials and Methods

The solutions of poly(butylcarbosilane) (PBCS) dendrimer (from the third up to seventh generations) with deuterated chloroform, poly(allylcarbosilane) (PACS) dendrimer (from the fifth up to seventh generations) with the same solvent [43] and solutions of poly(amidoamine) dendrimer (from the third and fourth generations) with hydroxyl surface groups (PAMAM-OH) with methanol were studied.

Macromolecules of PBCS and PACS were synthesized in the Laboratory of Organoelement Polymer Synthesis at the Enikolopov Institute of Synthetic Polymer Materials of the Russian Academy of Sciences. The synthesis of similar polycarbosilane dendrimers was reported in refs. 45 and 46. To illustrate the dendrimer structure, the second-generation macromolecules of PBCS and PACS dendrimers are depicted in Fig. 3a and b, respectively. The polydispersity index of these macromolecules is $M_w/M_n \cong 1.001$. As seen in Fig. 3a and b, the structures of dendrimers of these two families are different. In particular, the PACS dendrimer has a tri-functionality core and allyl surface groups, the PBCS dendrimer has a tetra-functionality core and butyl surface groups. In accord with basic ideas about the dendrimer properties [4], the dendritic matrix of PBCS should be characterized by a higher density of its monomeric units as compared to PACS macromolecules due to the higher functionality of the macromolecular core. Thus, we may test PFG NMR for providing information about the interior structure of the dendritic matrix (in particular, about the density of the studied macromolecules' own monomeric units) by comparing results obtained for PBCS and PACS. The initial solutions of PAMAM-OH dendrimers with methanol were received from Sigma-Aldrich Corporation. The sketch of the second-generation macromolecule of PAMAM-OH is depicted in Fig. 3c. The PAMAM-OH macromolecule has a tetra-functionality core as has the PBCS macromolecule. However, the chemical nature of repeat units and terminal groups of PAMAM-OH is essentially different from that of PACS and PBCS dendrimers.

The characterizations of PBCS and PACS macromolecules and PAMAM-OH dendrimers and their solutions are given in Table 1.

The D values of PBCS and PACS were measured on a spectrometer operating at the ^{1}H resonance frequency of 64 MHz (Kazan State University, Russian Federation). The maximum amplitude of the PFG $g_{max} = 30$ T/m. The duration of PFG δ was varied from 0.087 up to 2.5 ms, the time delay between the first and second 90° rf pulses was from 1.5 up to 5.0 ms, the value of the diffusion time $t_d = \Delta - \delta/3$ (here Δ is a delay between the pulses of the field gradient,

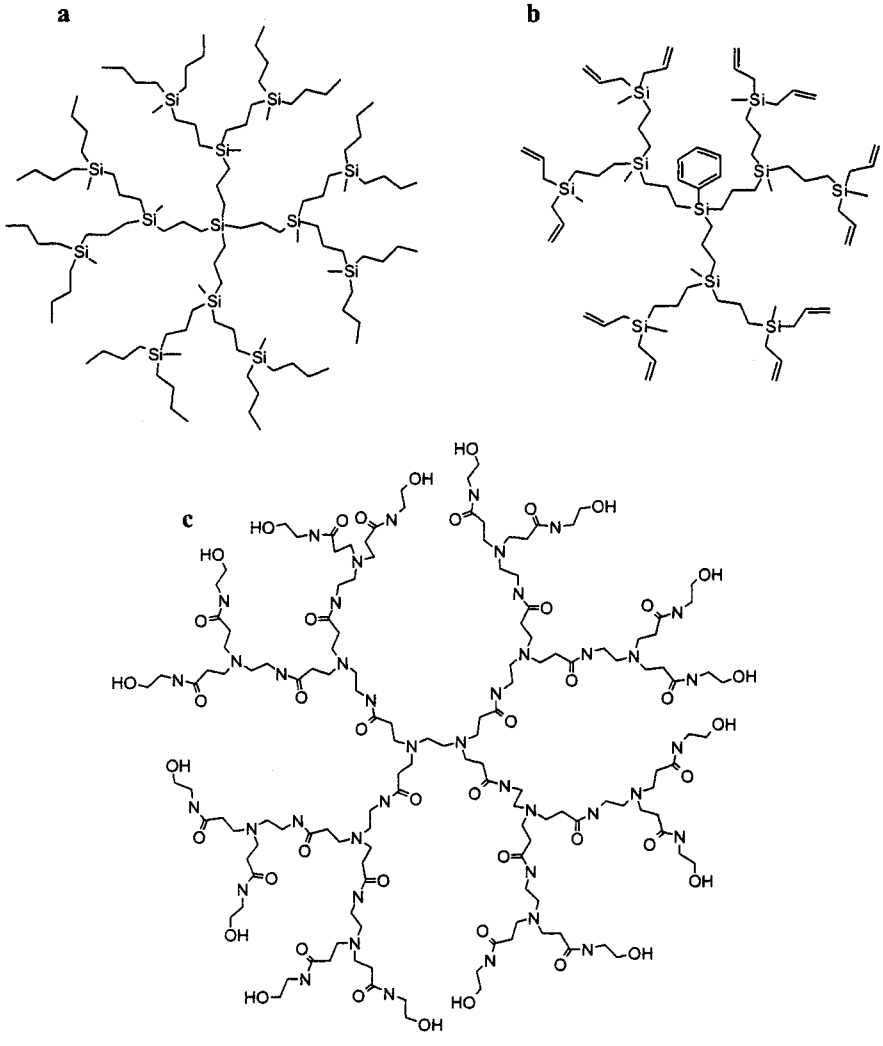

Fig. 3. Sketches of the second-generation macromolecules ($G = 2$) for: **a** poly(butylcarbosilane) dendrimer, PBCS; **b** poly(allylcarbosilane) dendrimer, PACS; and **c** poly(amido amine) dendrimer with hydroxyl surface groups.

see Fig. 2), was varied from 7 up to 700 ms, depending on the experimental conditions. The times of longitudinal (T_1) and transverse (T_2) NM relaxation times of polycarbosilane dendrimers were measured on a spectrometer operating at the ^{1}H resonance frequency of 19.8 MHz. In order to study T_2-relaxation processes, the Carr-Purcell-Meiboom-Gill (CPMG) sequence was employed, the spin-lattice relaxation was studied by the original "one-scan" [47] multipulse sequence for

Table 1. Dendrimers and their solutions.

Dendrimer	Generation number, G	Designation of dendrimer	Molecular weight, M_w (g/mole)	Range of the dendrimer volume fraction in solutions
PBCS	3	PBCS 3	4299	0.036–0.71
	4	PBCS 4	8946	0.038–0.70
	5	PBCS 5	17900	0.034–0.66
	6	PBCS 6	36122	0.027–0.70
	7	PBCS 7	72536	0.041–0.59
PACS	5	PACS 5	11831	0.01–0.57
	6	PACS 6	23952	0.01–0.62
	7	PACS 7	48336	0.01–0.53
PAMAM-OH	3	PAMAM-OH 3	6941	0.001–0.48
	4	PAMAM-OH 4	14279	0.001–0.45

measuring T_1. The measurements of D, T_1 and T_2 of PBCS were conducted at the temperature (25±1)°C, and those for PACS dendrimers at (30±1)°C [43].

To study the self-diffusion and NM relaxation of PAMAM-OH dendrimers the NMR spectrometers Bruker AVANCE 300 and Bruker AVANCE 500 operating at the ^{1}H resonance frequency of 300 and 500 MHz, respectively (Institute for Polymer Research Dresden, Germany) [48] were used. The transverse relaxation times T_2 were measured by the CPMG sequence at the ^{1}H frequency of 300 MHz. The diffusion measurements were performed by PFG NMR on both spectrometers. To this end, the Bruker AVANCE 300 spectrometer was equipped by a microimaging Bruker Micro2.5 accessory generating the maximal PFG amplitude g_{max} of up to 1 T/m; and the Bruker AVANCE 500 spectrometer was employed with a Diff30 diffusion probe with g_{max} = 12 T/m. Depending on the dendrimer concentration in the solution, the τ value was varied from 4.5 up to 13 ms, the δ value from 0.70 up to 10.5 ms, the Δ value was changed from 50 up to 500 ms. All NMR experiments with PAMAM-OH solutions were carried out at (20.0±0.2)°C.

For all three families of the dendrimers studied, the DDs of the spin-echo signal were obtained as the functions of the square of the PFG amplitude g^2 with all other time parameters of the given sequence being constant.

The uncertainty of D, T_1 and T_2 measurements made for dendrimers was not higher than 10% at the worst.

3 Results and Discussion

3.1 Diffusion Decays for the Dendrimer-Solvent Systems

The typical DDs obtained for the polycarbosilane (PBCS and PACS [43]) solutions with deuterated chloroform are presented in Fig. 4a and b. One can see that all DDs have a simple exponential shape and can be described by Eq. (1), if the number of the system components equals 1 [29, 34]:

$$\frac{A(\gamma^2 g^2 \delta^2 t_d)}{A(0)} = \exp(-\gamma^2 g^2 \delta^2 D t_d) . \quad (2)$$

The D values have been determined from the slope of the corresponding DD curves. It should be noted that for PBCS 3, 4, 5, and 7 macromolecules, as

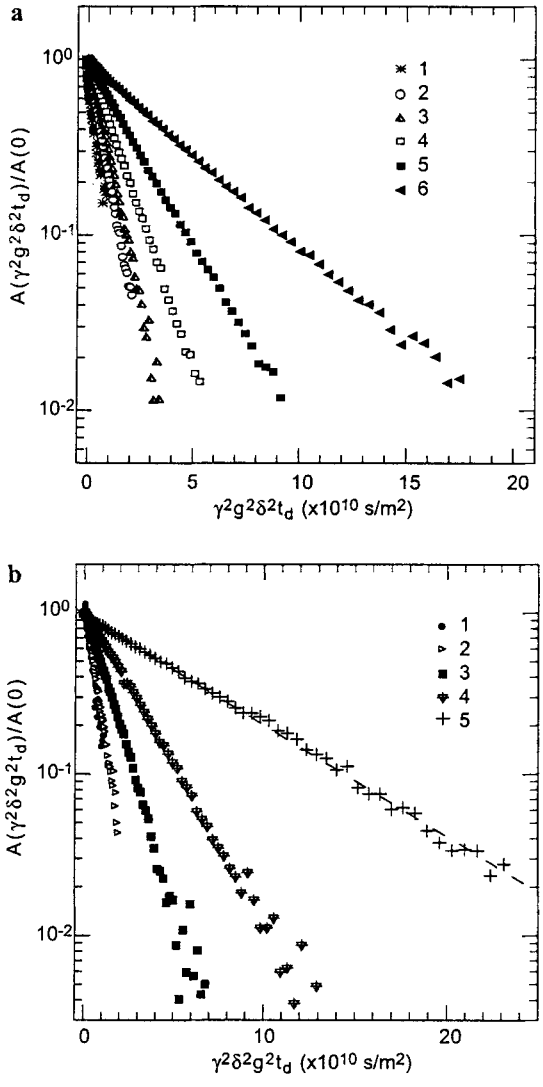

Fig. 4. Typical DDs characterizing diffusion of polycarbosilane dendrimers in solutions with deuterated chloroform; **a** DDs for PACS 5 in solutions with the dendrimer volume fraction, φ: 0.01 (1), 0.10 (2), 0.14 (3), 0.21 (4), 0.27 (5), 0.33 (6) [43]; **b** DDs for PBCS 6 in solutions with the dendrimer volume fraction, φ: 0.027 (1), 0.053 (2), 0.155 (3), 0.24 (4), 0.35 (5).

well as for PACS 6 and 7 [43], DDs analogous to those in Fig. 4 have been detected.

As mentioned above, the self-diffusion and relaxation of PAMAM-OH macromolecules were studied on NMR spectrometers allowing the Fourier transformation of the NMR signal and obtaining the high-resolution spectra. Figure 5 shows a sketch of the PAMAM-OH 3 dendrimer (Fig. 5a) and the proton NMR spectrum detected for this dendrimer in the solution with deuterated methanol (Fig. 5b). Note that the spectral lines corresponding to the protons of methyl groups denoted by symbols 2, 2′, 2″, 2‴, 3, 3′, 3″, 3‴, and 4, 4′, 4″, 5, 5′, 5″ in Fig. 5a cannot be resolved as separate spectrum lines. Therefore in Fig. 5b, the signals of the corresponding lines are marked by symbols 2, 3, 4, and 5, respectively. The NMR spectrum (Fig. 5b) has been used to identify the dendrimer lines in the experiments on measuring the transverse and longitudinal relaxation times and D of PAMAM-OH in solutions with methanol.

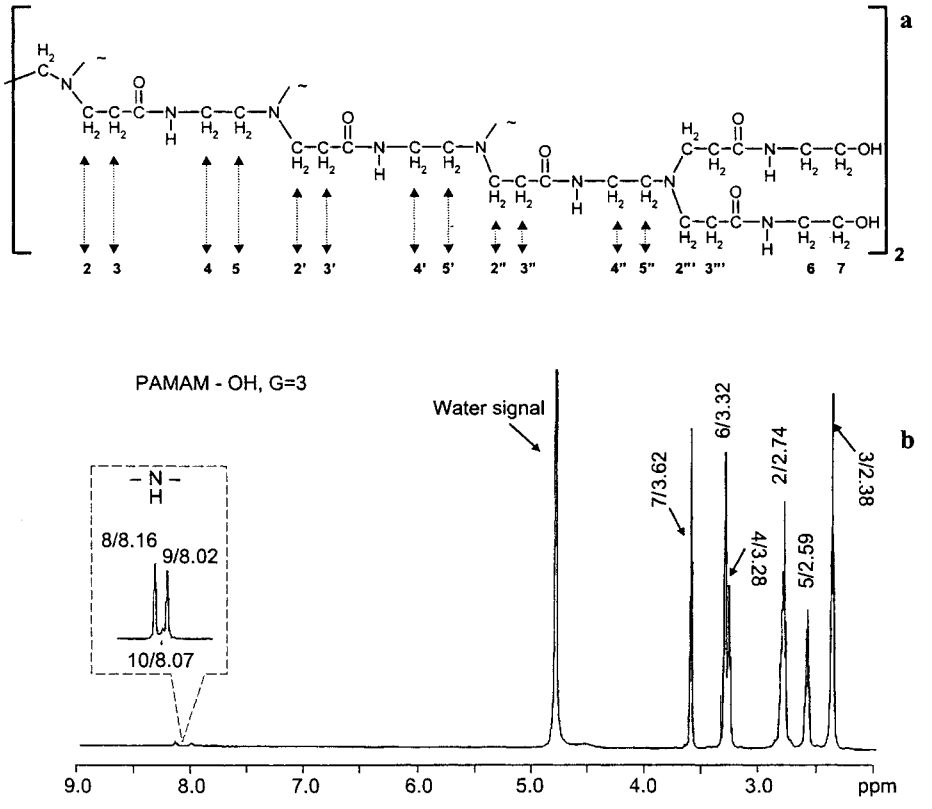

Fig. 5. **a** Molecular structure of PAMAM-OH 3; **b** ^{1}H NMR spectrum of PAMAM-OH 3 dissolved in deuterated methanol (dendrimer volume fraction, 1 g/l) obtained on a spectrometer operating at the proton resonance frequency of 500 MHz.

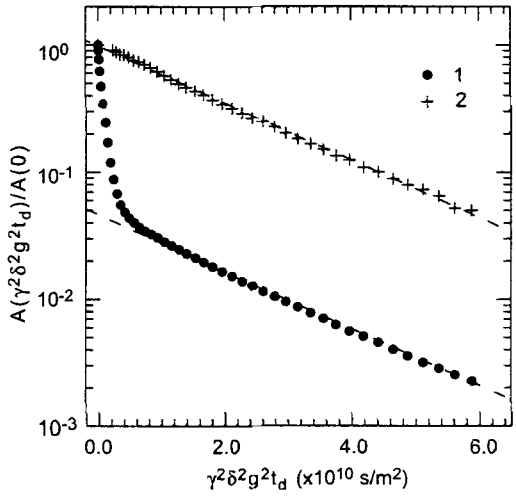

Fig. 6. DDs obtained for lines with numbers 7 (3.6 ppm, curve 1) and 8 (8.2 ppm, curve 2) in the NMR spectrum of PAMAM-OH 3, diluted in methanol ($\varphi = 0.053$).

The typical DDs corresponding to the macromolecules in the PAMAM-OH-methanol systems are shown in Fig. 6. The curves obtained may be separated into two types: so-called single-exponential [30] (Fig. 6, curve 1) and double-exponential (Fig. 6, curve 2) DDs. The single-exponential DDs have been obtained for spectral lines 2 (2.7 ppm), 3 (2.4 ppm), 5 (2.6 ppm), 8 (8.2 ppm) and 9 (8.0 ppm) (see Fig. 5). The double-exponential curves of DDs have been detected for lines 6 (3.3 ppm) and 7 (3.6 ppm). Within this range of the NMR spectrum (the chemical shift from 4 up to 5 ppm), the intensive enough lines of methanol are located. The weak dendrimer signals appear on the wide wings of the strong solvent signals. The presence of the solvent signal sufficiently affects the shape of DDs obtained for the spectrum lines 6 and 7 leading to the complicated, nonexponential form of curves. The shape of these DDs is satisfactorily described by the expression of the type (1), which contains, in the right-hand side, two exponential terms characterizing diffusivity of dendrimer and solvent [29, 34], respectively:

$$\frac{A(\gamma^2\delta^2 g^2 t_d)}{A(0)} = p_d \exp(-\gamma^2\delta^2 g^2 D_d t_d) + p_s \exp(-\gamma^2\delta^2 g^2 D_s t_d),$$

here p_d and p_s are the relative parts of protons belonging to dendrimer and methanol, respectively; D_d and D_s are the dendrimer and solvent diffusion rates, respectively. To calculate the value of the dendrimer D, the double-exponential DD was resolved into two exponential components [29, 34], and the rates D of dendrimer and methanol were determined from the slopes of these components.

Single-exponential DDs obtained for PAMAM-OH solutions with the various dendrimer content are shown in Fig. 7. The shape of DDs, as in the case of

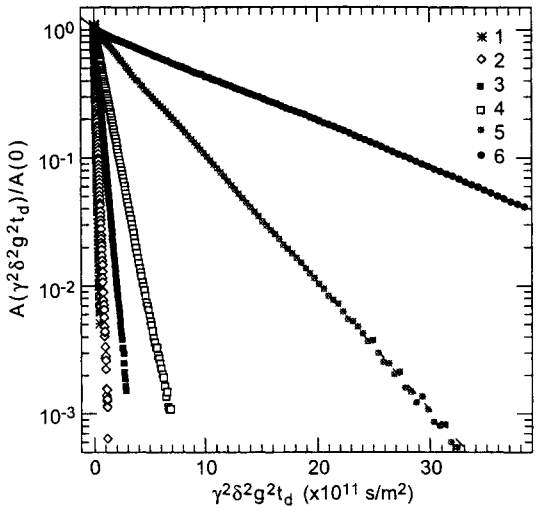

Fig. 7. DDs characterizing diffusion of PAMAM-OH 3 (spectrum line 2, 2.74 ppm) in the methanol solutions with the dendrimer volume fraction φ: 0.077 (1), 0.152 (2), 0.235 (3), 0.324 (4), 0.418 (5), 0.48 (6).

polycarbosilane dendrimers, is described by the single-component equation of the type (2) independent of the polymeric concentration.

Thus, the result of the analysis of the diffusion decays obtained for PBCS, PACS and PAMAM-OH conforms to ideas about the narrow enough molecular-mass distribution of dendrimers. It was also observed that the shape of DDs does not depend on the diffusion time t_d. This means that there are no reasons to talk about the existence of macromolecular associations, which could exist as the analogous formations (clusters) present in solutions of linear flexible chain polymers [38–40, 42], in the dendrimer solutions studied.

3.2 Concentration Dependences of Dendrimer Diffusion Rates

The experimental concentration dependences of macromolecular diffusion rates obtained for the dendrimer-solvent systems studied are shown in Fig. 8. In the concentrated-solution range ($\varphi > 0.4$) these dependences are not described within the frames of the free-volume theory [32] as in the case of poly(propylene imine) dendrimers of fourth and fifth generations reported in ref. 28. It is reasonable to assume that the free-volume theories, as conceptions developed on the basis of statistical physics, cannot adequately characterize the diffusion behavior of polymers in concentrated solutions because in this case the dynamic interactions between polymeric matrices (for instance, the engagements and penetrations) dominantly influence the macromolecular self-diffusion. As noted in refs. 28, 38, and 44, it is impossible to obtain a complete description of

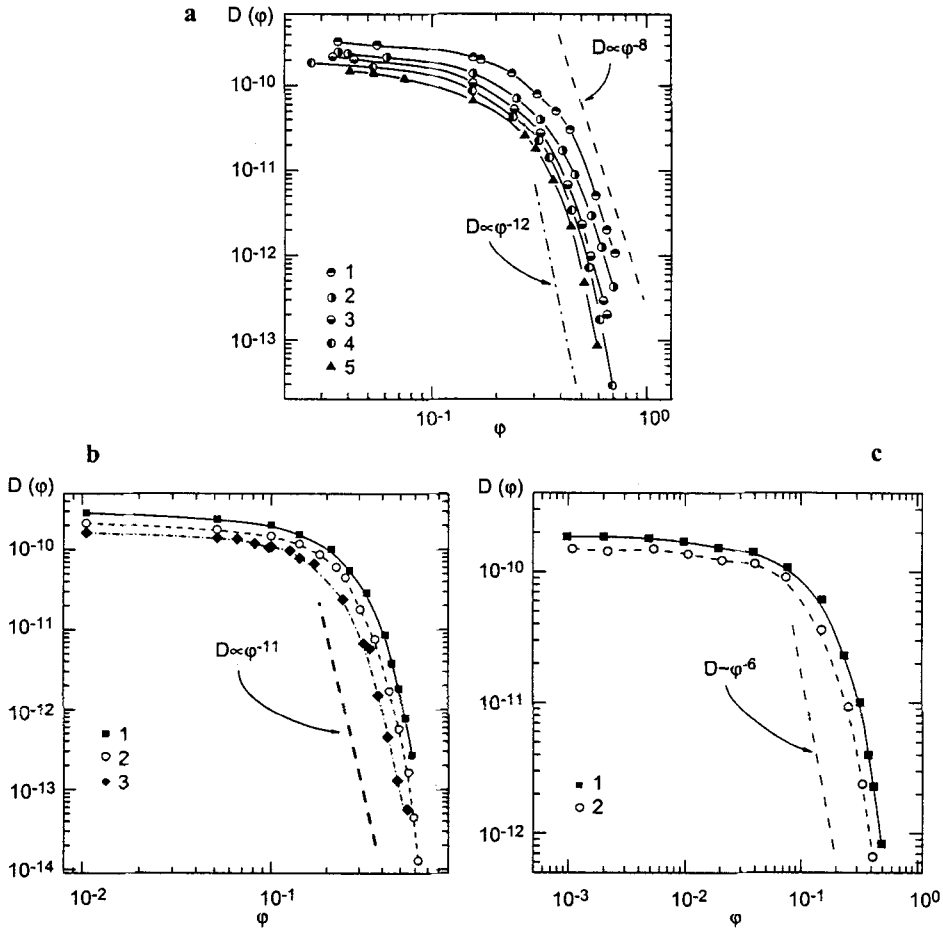

Fig. 8. Concentration dependences obtained for: **a** PBCS 3 (1), 4 (2), 5 (3), 6 (4), 7 (5) in the deuterated chloroform solutions; **b** PACS 5 (1), 6 (2), 7 (3) in the deuterated chloroform solutions [43]; **c** PAMAM-OH 3 (1), 4 (2) in the methanol solutions [48].

the polymeric translational mobility by the use of statistical-physics principles only; and a more successful solution of this problem may be found within the frames of dynamic theories of macromolecules. Nevertheless, it is easy to observe (Fig. 8) that all obtained curves plotted in the coordinate axes log$D$ vs. logφ are similar: within the limits of dilute solutions (at $\varphi \to 0$) they tend to a certain constant value of the diffusion rate, $D_0 = \lim_{\varphi \to 0} D(\varphi)$, and in the concentrated-solution range the dependence $D(\varphi)$ may be satisfactorily described by a general power relation:

$$D(\varphi) \propto \varphi^{-\alpha(\varphi)}, \tag{3}$$

where the exponent α is the function of the dendrimer concentration and, as seen in Fig. 8, in general depends on individual features of the dendrimer-solvent system.

The concentration dependence of the macromolecular D may be also described within the frames of de Gennes dynamic scaling theory [44] through Eq. (3). In this case, at least two characteristic asymptotes are distinguished: within the limits of extremely dilute solutions ($\varphi \to 0$) and in the range of concentrated solutions of polymers ($\varphi \to 1$). These asymptotes are determined by Eq. (3) with $\alpha = 0$ at $\varphi \to 0$ and $\alpha = 3$ at $\varphi \to 1$. The concentration dependence of normalized diffusion rates of macromolecules, which was obtained for various linear polymer-solvent systems [29, 40, 42], can be regarded as an experimental confirmation of the dynamic scaling theory. This dependence is plotted in the coordinate frames with dimensionless axes $\log(D'(\varphi)/D_0)$ vs. $\log(\varphi/\hat{\varphi})$, where D_0 is the diffusion rate of macromolecules in the extremely dilute solution; D' is the normalized macromolecular diffusion rate obtained from the equation:

$$D'(\varphi) = D(\varphi)/L(\varphi), \tag{4}$$

$L(\varphi)$ is the normalizing function taking into account information about changes of the chain dynamics as the polymeric concentration increases; $D(\varphi)$ is the measured diffusion rate of macromolecules in the solution with the polymer content φ. The quantity $\hat{\varphi}$ is a critical concentration of macromolecules at which the polymers begin to overlap. At $\varphi > \hat{\varphi}$, the interactions between macromolecules dominantly influence the self-diffusion of polymers. The $\hat{\varphi}$ value is obtained [40] as a crossover of asymptotes with $\alpha = 0$ at $\varphi \to 0$ and $\alpha = 3$ at $\varphi \to 1$ for the dependence $D'(\varphi)$. The normalizing procedure (Eq. (4)) is employed both to take into account the changes of the monomer local mobility as the macromolecular concentration increases and to eliminate the effect of individual features of inter- and intramolecular interactions in the polymer-solvent system in the analysis of results [29, 38, 40]. In terms of the polymeric chain correlation times τ_c, characterizing the local mobility of monomers, the $L(\varphi)$ function can be defined as $L(\varphi) = \overline{\tau}_c(0)/\overline{\tau}_c(\varphi)$ [29], where $\overline{\tau}_c(0) = \lim_{\varphi \to 0} \overline{\tau}_c(\varphi)$ and $\overline{\tau}_c(\varphi)$ are the mean correlation times of polymer in an extremely dilute solution and in solution with the polymer content φ, respectively. In practice, it is impossible to obtain a general expression for the L function due to the variety of dynamic interactions in the system studied. In other words, it is necessary to find an individual $L(\varphi)$ function for each polymer-solvent system. In order to define this function, it was suggested [40] to perform the independent measurements of the nuclear magnetic relaxation times T_1 or T_2 of polymers. In the simplest case, when, for example, $\overline{\tau}_c \ll T_2$ holds and the relaxation is measured in a so-called high-temperature regime, the relations $T_2 \propto \overline{\tau}_c^{-1}$ and $T_1 \propto \overline{\tau}_c^{-1}$ are valid for polymers. Finally, the L function can be determined from the experimental dependences $T_1(\varphi)$ or $T_2(\varphi)$ as follows:

$$L(\varphi) = \overline{\tau}_c(0)/\overline{\tau}_c(\varphi) = T_1(\varphi)/T_1(0), \tag{5}$$

or

$$L(\varphi) = \bar{\tau}_c(0)/\bar{\tau}_c(\varphi) = T_2(\varphi)/T_2(0)\,,$$

where $T_2 = \lim_{\varphi \to 0} T_2(\varphi)$ and $T_1 = \lim_{\varphi \to 0} T_1(\varphi)$, $T_2(\varphi)$ and $T_1(\varphi)$ are the transverse and longitudinal NM relaxation times of polymer in an extremely dilute solution and in a solution with the polymer content φ, respectively.

It is also necessary to note that the above approach to analyzing dependences $D(\varphi)$ of polymers [40] was successfully applied to describe the self-diffusion of globular proteins in aqueous suspensions [49] and led to obtaining the corresponding empirical generalized concentration dependence $D'(\varphi)$ for proteins.

In order to describe the obtained concentration dependences of the dendrimer diffusion rates within a general approach, let us consider the procedure of obtaining $L(\varphi)$ functions for the dendrimer-solvent systems studied.

3.3 Features of Polycarbosilane Dendrimer NM Relaxation: Normalizing Functions

The T_1 relaxation attenuations of magnetization obtained for polycarbosilane dendrimers of PBCS and PACS [43] families in solutions on a spectrometer operating at the proton resonance frequency of 19.8 MHz, are shown in Fig. 9 by the example of solutions of PBCS 6 with the dendrimer contents $\varphi = 0.24$ and $\varphi = 0.54$. These relaxation curves have a complex nonexponential shape and are characterized by a spectrum of T_1 times.

The existence of a spectrum of relaxation times may be explained, firstly, by the presence of nonequivalent protons in the dendrimer cell structure and, secondly, by the possible difference of the mobility of protons belonging to the same chemical groups but located on the different dendrimer cascades. The difference of the macromolecular spin-lattice relaxation times corresponding to protons of different chemical groups can be easily observed by comparing the curves of the magnetization recovery obtained for different lines of the NMR spectrum depicted in Fig. 10a. The curves shown here were detected for the solution of PACS 5 with deuterated chloroform ($\varphi = 0.1$) with the magnetization inversion-recovery method on an NMR spectrometer operating at the ^{1}H resonance frequency of 500 MHz. As seen in Fig. 10a, the recovery curves corresponding to different chemical groups cross the zero-amplitude point at different time moments. The nonexponential shape of the curves shown in Fig. 10b allowed the hypothesis that the mobility of the branches of the dendrimer matrix differs depending on their remoteness from the dendrimer core. In particular, it was found that the shape of curves obtained for methylene and methyl groups of PACS dendrimers cannot be described by a single-exponential function of the type $A(t) = A(0)[1 - 2\exp(-t/T_1)]$, where $A(t)$ and $A(0)$ are the NMR signal amplitudes detected at the time moment t and at the start time, respectively; T_1 is the characteristic longitudinal relaxation time for the given system of spins. In Fig. 10b, the relaxation curves have been replotted as a

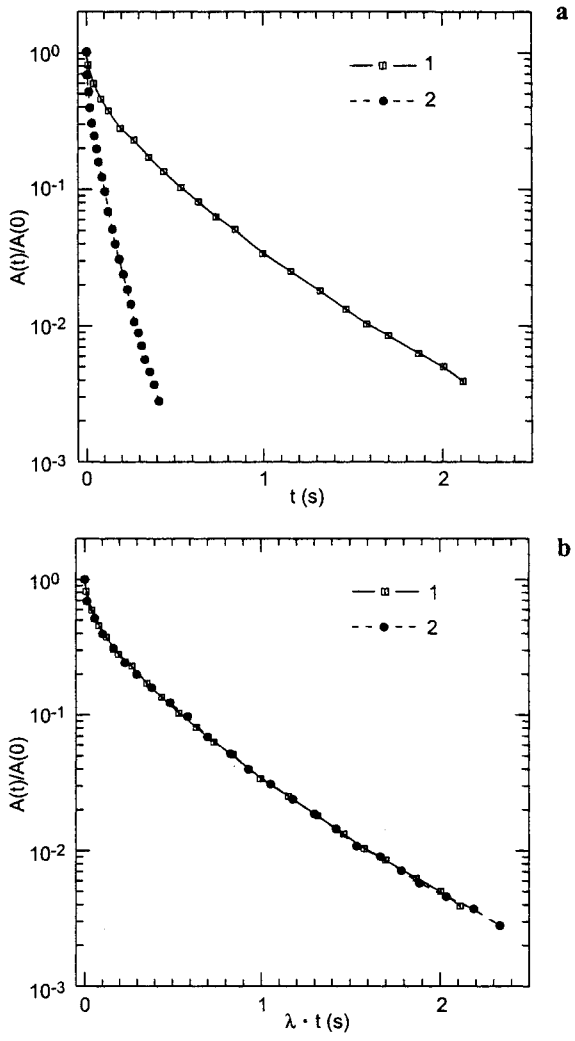

Fig. 9. **a** T_1 relaxation attenuations of macroscopic magnetization of PBCS 6 in solutions with macromolecular concentration $\varphi = 0.24$ (curve 1) and $\varphi = 0.54$ (curve 2); **b** the same relaxation attenuation curves replotted in the coordinate frames with the scaled abscissa axis; scaling coefficient $\lambda = 1$ for curve 1 and $\lambda = 5.67$ for curve 2.

functions of the type $\Psi(t) \equiv A(t)/2A(0) = \sum_j p_j \exp(-t/T_{1j})$, and these attenuations, in turn, are characterized by a spectrum of T_1 times. This result may serve as an indirect evidence that the mobility of the dendritic matrix junctions differs depending on their remoteness from the macromolecular core. In order to study this feature of the microscopic mobility of dendritic matrix in solvent in detail, it is necessary to prepare special macromolecules with deuterated cascades.

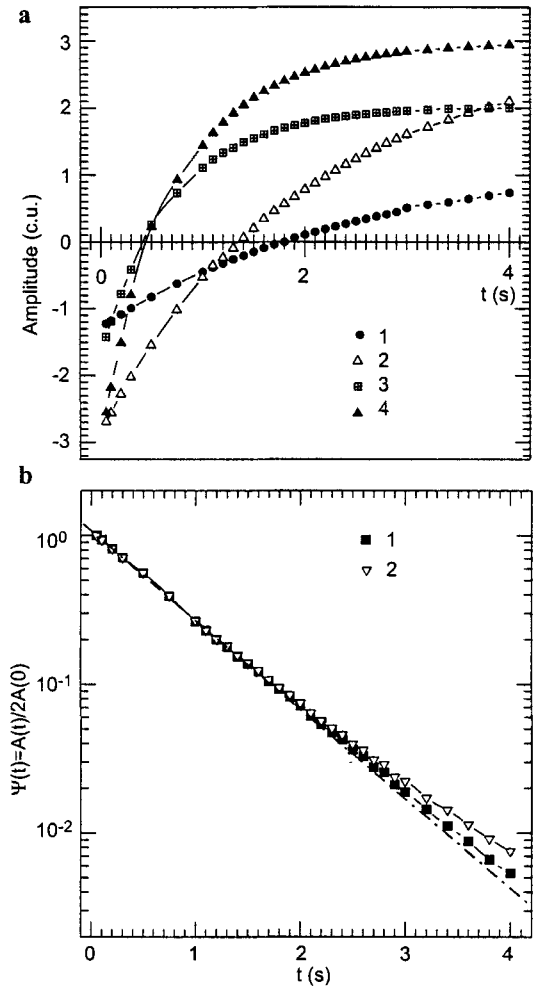

Fig. 10. T_1 relaxation curves obtained for solutions of PACS 5 with deuterated chloroform at $\varphi = 0.1$, by the inversion-recovery method on a spectrometer operating at the proton resonance frequency of 500 MHz. **a** The recovery curves of magnetization for protons of metin (1) and methylene (2) groups located in the terminal groups of dendrimer, and for methylene (3) and methyl (4) groups composing the repeat units of PACS 5; **b** the recovery curves obtained for protons of methylene (1) and methyl (2) groups of repeat units PACS 5; this figure shows the nonexponential form of these curves, the dashed-dotted line is plotted by the exponential law and exhibits the initial slope of relaxation curves presented here.

To obtain the L functions, it should be noted that if a spectrum of T_1 relaxation times exists, there is an uncertainty in the choice of a component from the spectrum of T_1 necessary to define and plot the L function. This problem could be simplified, if all T_{1i} values in the spectrum of longitudinal relaxation times varied in the same manner as the dendrimer concentration increased in the solution. In this case the normalizing functions could be obtained from the con-

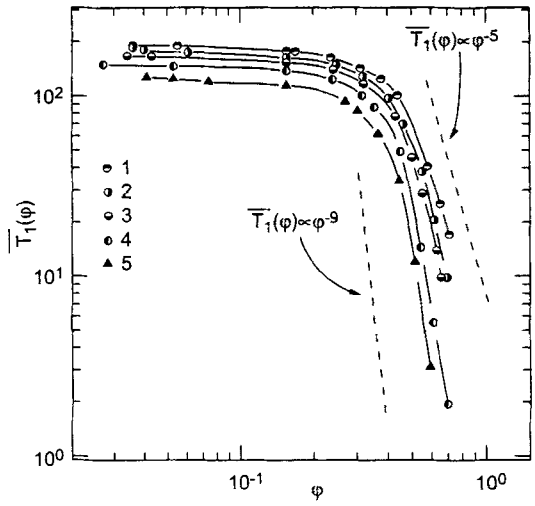

Fig. 11. Concentration dependences of the mean spin-lattice relaxation times for PBCS 3 (1), 4 (2), 5 (3), 6 (4), 7 (5).

centration dependences of an arbitrary component of the spectrum of longitudinal relaxation times, $T_{1i}(\varphi)$, in accord with Eq. (5).

Let us turn to the relaxation attenuations depicted in Fig. 9 and show that in our case this condition holds. In Fig. 9b we have compared two relaxation curves obtained for the solutions with different dendrimer concentrations. The abscissa axis of the frames plotted in Fig. 9b has been rescaled by the coefficient λ, so that $\lambda = 1$ for the relaxation curve 1. For the curve 2 this coefficient has been chosen to provide the best coincidence of these two curves and, as a result, it turned to be 5.67. As seen in Fig. 9b, over the whole range of the change of signal amplitudes both relaxation attenuations coincide completely. It proves that all components T_{1i} of the spectrum decrease in the same manner, as the dendrimer concentration increases in the solution. Thus, the L function can be defined by the concentration dependence of an arbitrary T_{1i} of the spectrum of relaxation time as well as by the concentration dependence of the mean time of longitudinal relaxation, $\overline{T}_1(\varphi)$. The use of $\overline{T}_1$ seems to be more correct because the mean time characterizes the whole spectrum (in accord with the definition $\overline{T}_1^{-1} = \sum_i p_i T_{1i}^{-1}$, where p_i is the relative part of spins relaxing with a characteristic time T_{1i}) and may be always determined from the initial slope of the relaxation attenuation curve with an adequate accuracy.

Finally, the $L(\varphi)$ function can be obtained from the measurements of $\overline{T}_1(\varphi)$:

$$L(\varphi) = \overline{T}_1(\varphi)/\overline{T}_1(0)\,,$$

where $\overline{T}_1(\varphi)$ and $\overline{T}_1(0)$ are the mean longitudinal relaxation times of dendrimers in the solution with the macromolecular content φ and in the extremely dilute solu-

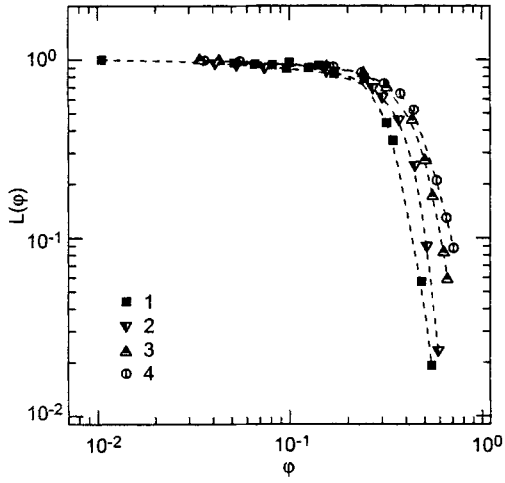

Fig. 12. Normalizing functions obtained for dendrimers: PBCS 3 (1), PBCS 5 (2), PBCS 7 (3) and PACS 7 (4).

tion ($\varphi \to 0$), respectively. As an example, the concentration dependences of the mean longitudinal relaxation times of PBCS dendrimers are presented in Fig. 11.

It is necessary to note that for dendrimers of PACS 5, 6, 7 [43] and for macromolecules of PBCS 3, 4, 5, 7 the study of the macromolecular longitudinal relaxation has led to results analogous to those obtained and discussed above for solutions of dendrimer PBCS 6.

Some normalizing L functions defined for macromolecules of families of PBCS, PACS and PAMAM-OH dendrimers are shown in Fig. 12. It should be noted that the normalizing functions $L(\varphi)$ may be determined from the concentration dependences of the mean transverse relaxation times of the dendrimers, $\overline{T}_2(\varphi)$. For PBCS and PACS such functions do not differ from those obtained from measuring $\overline{T}_1(\varphi)$.

3.4 PAMAM-OH Dendrimers: NM Relaxation Features and Normalizing L Functions

The spin-spin relaxation times of PAMAM-OH dendrimers were measured at the ^{1}H resonance frequency of 300 MHz with a CPMG pulse sequence [48]. The spin system evolution times (delay between the first 90° and 180° pulses and the half of delay between the following 180° pulses), τ, in the sequence was varied from 75 up to 4500 μs. The spin echo amplitude was measured for the second echo and then for every fourth one.

Several dependences $T_2(\varphi)$ obtained for protons of different chemical groups of PAMAM-OH 4 [48] are shown in Fig. 13. In order to obtain the normalizing function for PAMAM-OH dendrimers, it is possible to use, as found, any of dependences $T_2(\varphi)$ obtained. This is demonstrated in Fig. 14 with the concentra-

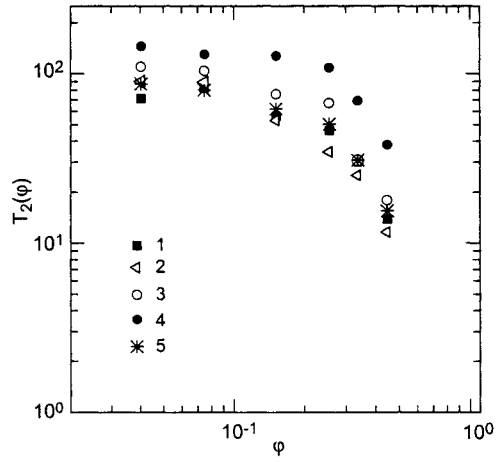

Fig. 13. Concentration dependences of PAMAM-OH 4 spin-spin relaxation times [48] obtained for lines with the following position in the NMR spectrum (see also Fig. 5): 2.74 ppm (1), 2.59 ppm (2), 2.38 ppm (3), 8.2 ppm (4), 8.0 ppm (5).

tion dependences of the normalized transverse relaxation times of the dendrimers plotted in the frames $\log[T_2(\varphi)/T_2(0)]$ vs. $\log\varphi$, where $T_2(0) = \lim_{\varphi \to 0} T_2(\varphi)$. It is seen that normalized dependences $T_2(\varphi)$ obtained for protons of different parts of the dendritic macromolecule coincide with an adequate accuracy.

For transverse NM relaxation of the PAMAM-OH 3 macromolecules in solutions, results analogous to those for PAMAM-OH dendrimer were derived. The

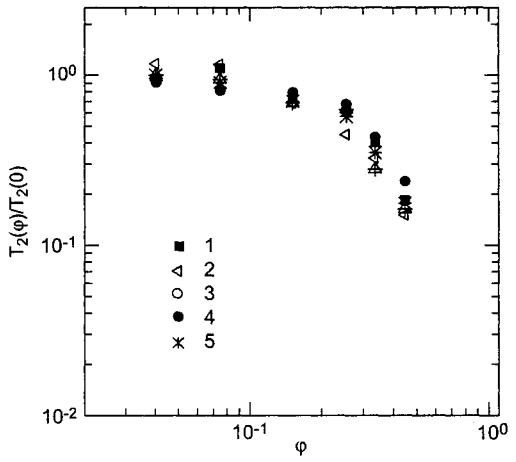

Fig. 14. Normalized concentration dependences of PAMAM-OH 4 spin-spin relaxation times [48] obtained for lines with the following position in the NMR spectrum (see also Fig. 5): 2.74 ppm (1), 2.59 ppm (2), 2.38 ppm (3), 8.2 ppm (4), 8.0 ppm (5).

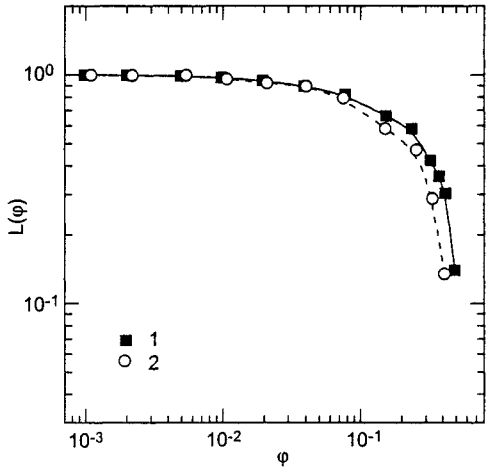

Fig. 15. Normalizing functions defined for PAMAM-OH 3 (1), 4 (2) [48].

normalizing $L(\varphi)$ functions of PAMAM-OH 3 and 4 dendrimers are shown in Fig. 15.

3.5 The Generalized Concentration Dependence of Normalized Diffusion Rates of Dendrimers

The experimental concentration dependences of the dendrimer diffusion rates (Fig. 8) have been reduced by L functions corresponding to each dendrimer generation in accord with Eq. (4). This procedure resulted in obtaining the dependences $D'(\varphi)$. Several such curves obtained for macromolecules PBCS 3, PACS 5 and PAMAM-OH 4 plotted within the frames $\log(D'(\varphi)/D_0)$ are presented in Fig. 16.

As seen in Fig. 16, each of the concentration dependences $D'(\varphi)$ is characterized by two asymptotes; they may be described with Eq. (3), if $\alpha = 0$ for an asymptote at the limit of dilute solutions ($\varphi \to 0$) and $\alpha = 3$ for the concentrated-solution range. The crossover of these asymptotes formally provides the value of the critical concentration $\hat{\varphi}(M)$ [40]. The values have been defined in this manner for all dendrimers studied (PBCS, PACS, PAMAM-OH). As a result, for families of polycarbosilane dendrimers the M dependences containing information about microscopic features of dendritic matrix imbedded into the solvent have been obtained. These dependences are discussed below.

The concentration dependences of the dendrimer diffusion rates are replotted within the frames $\log(D'(\varphi)/D_0)$ vs. $\log(\varphi/\hat{\varphi})$ and shown in Fig. 17. In these coordinates, it is possible to unite the dependences $D'(\varphi)$ obtained for all dendrimer-solvent systems studied and, as a result, to obtain the generalized concentration dependence of the normalized diffusion rates of dendrimers.

This dependence permits one to talk about common regularities of the diffusion behavior of different symmetrical dendrimers in solutions. The result pre-

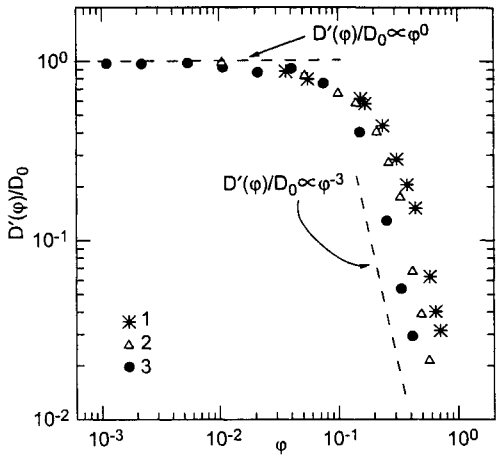

Fig. 16. Curves of concentration dependences of the dendrimer self-diffusion coefficients reduced by the L functions and magnitude D_0; curves for PBCS 3 (1), PACS 5 (2) and PAMAM-OH 4 (3) are shown.

sented in Fig. 17 allows one to state that the individual dendrimer features (such as molecular weight, functionality of core, structure and nature of the repeat units and terminal [surface] groups) practically do not affect the character of the discussed regularities of the dendrimer self-diffusion. The differences of the solvent properties and the different temperature of solutions (at least, for the dendrimer-solvent systems studied here) also do not affect the shape of the generalized concentration dependence of the dendrimer rates D' within the limits of the macromolecular concentrations and molecular weights studied.

The universal concentration dependence of macromolecular diffusion rates obtained for solutions of linear flexible-chain polymers [29, 30, 38, 40, 42] and the generalized concentration dependence of the normalized diffusion rates of globular proteins in aqueous suspensions [49] are also presented in Fig. 17 for comparison. This comparison shows that the generalized concentration dependence obtained for dendrimers coincides with the universal dependence for linear polymers only within the limits of dilute solutions and in the concentrated-solution range. Within the intermediate range of the macromolecular concentrations these two curves are significantly different, evidencing that the diffusion behavior of dendrimers and the linear polymers differs. It may be explained by non-Gaussian conformation of the dendritic macromolecule [4] and, as a result, by the dendrimer interactions differing from those in the typical polymers.

One more type of polymers with a conformation considerably different from the coils of linear polymers is globular protein. In particular, the rigid globular structure of the peptide chain and, as a consequence, the features of the interchain dynamics differing from those for linear polymers determine the differences of self-diffusion of proteins and polymers in solutions [48]. These differences may be easily noticed by comparing the generalized concentration dependence of the

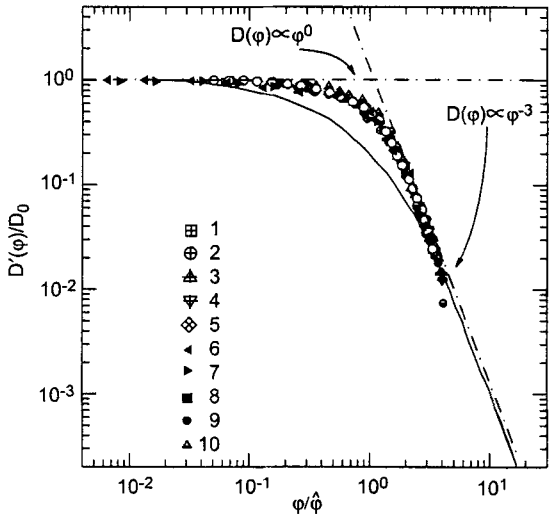

Fig. 17. Normalized concentration dependences of the reduced diffusion rates obtained for the dendrimers of PBCS 3 (1), 4 (2), 5 (3), 6 (4), 7 (5), PAMAM-OH 3 (6), 4 (7) [48] and PACS 5 (8), 6 (9), 7 (10) [43]. The generalized concentration dependence of the reduced coefficient D for globular proteins in aqueous suspensions (o) [49] and the universal concentration dependence of D for macromolecules in solutions of linear flexible-chain polymers (solid line) [40] have been also shown. The characteristic asymptotes are denoted by dashed-dotted lines.

normalized diffusion rates of proteins and the universal dependence for linear polymers depicted in Fig. 17. At the same time it is seen (Fig. 17) that curves of the generalized dependences obtained for the proteins and dendrimers coincide with an adequate accuracy over the whole concentration range studied. This result permits one to characterize the behavior of dendritic macromolecules as systems with interaction mechanisms similar to those for globular proteins. Thus, the absence of intermolecular entanglements and sufficient penetrations between the macromolecules should be seemingly stated as the basic features of self-diffusion of the dendrimers and globular proteins.

3.6 Molecular-Mass Dependences of the Dendrimer Critical Concentration

In order to determine the physical meaning of the value of the dendrimer critical concentration, $\hat{\varphi}$, the M dependences $\hat{\varphi}(M)$ obtained for polycarbosilane dendrimers have been analyzed. In accord with experimental data these dependences can be written down as follows:

$$\hat{\varphi}(M) \propto M^{-0.18\pm0.01} \tag{6a}$$

and

$$\hat{\varphi}(M) \propto M^{-0.104\pm0.005} \tag{6b}$$

for macromolecules of PACS and PBCS, respectively.

It is known that for suspensions of identical rigid spheres the value of the overlap concentration is independent of the particle molecular weight. In the case of the linear polymer solutions the dependence of the critical concentration of the coil overlap, $\hat{\varphi}(M)$, is determined by the relation [29, 40]

$$\hat{\varphi}(M) \propto M^{-0.50\pm0.03}.$$

Moreover, for polymer solutions with a Θ solvent the experimental dependences $\hat{\varphi}(M)$ coincide with the M dependences of the critical concentration φ^* introduced by de Gennes within the frames of the dynamic scaling theory [44] as the concentration at the beginning of the geometrical overlap of macromolecules. Conditionally φ^* separates the regions of dilute and semidilute nontangled solutions, and $\varphi^* \propto MR^{-3}(M)$; here R is the Flory radius or the hydrodynamic radius of a macromolecule. For the value of R the relation $R(M) \propto M^{\beta}$ holds. As a rule, the value of the β parameter changes from 0.5 up to 0.6 depending on the solvent quality in the solutions of the linear flexible-chain polymers [40]. The difference between the critical concentrations φ^* and $\hat{\varphi}$ is that the theoretical φ^* is determined by purely geometrical (statistical) arguments [44], while the experimental $\hat{\varphi}$ takes into account the influence of macromolecular interactions on the polymer translational dynamics [29, 40] in some matter, this leads to some difference between the M dependences of these concentrations in the case of a good solution. On the whole, the physical meaning of these concentrations is the same: they are the concentration of the overlap of the macromolecular coils.

If in the case of dendrimers $\hat{\varphi}$ has the meaning of the concentration at which the dendritic spheres begin to overlap, then one can try to obtain the M dependence of the dendrimer size. Let us assume that for dendrimers the relation $R(M)$ is also described by the scaling law $R(M) \propto M^{\beta}$, and for the dendrimer-solvent systems the dependence correlates with $R(M)$ in the same way as the overlap concentration $\varphi^* \propto MR^{-3}(M)$. Then for PACS and PBCS dendrimers the following relations are derived, respectively, with use of Eqs (6a) and (6b):

$$MR^{-3}(M) \propto M^{-0.18\pm0.01}$$

and

$$MR^{-3}(M) \propto M^{-0.104\pm0.005}.$$

Thus, within the limits of our assumptions the M dependences of the dendrimer size obtained for PACS and PBCS macromolecules are described, respectively, by the scaling relations

$$R(M) \propto M^{0.39\pm0.02} \tag{7a}$$

and

$$R(M) \propto M^{0.34\pm0.01}. \tag{7b}$$

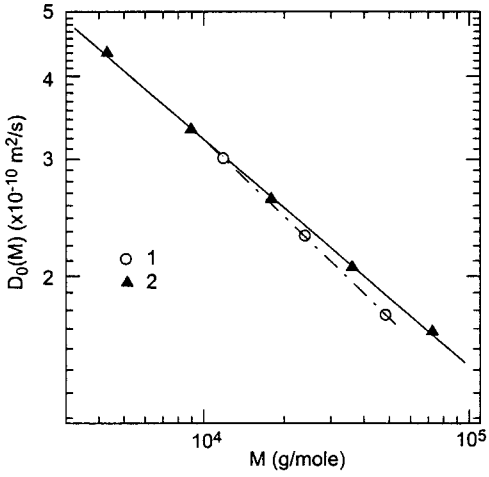

Fig. 18. M dependences of the diffusion rates obtained for PBCS (1) and PACS (2) [43] at the limit of an extremely diluted solution.

Equations (7a) and (7b) show that the values of the M exponent β are considerably lower than the values 0.5–0.6 corresponding to solutions of the linear flexible-chain macromolecules.

It should be noted that the dependences $R(M)$ may be obtained in a conventional manner by the calculation of the macromolecular hydrodynamic radius by the Stokes-Einstein formula and values of the diffusion rate of macromolecules in an extremely dilute solution, D_0. The M dependences of rates D_0 obtained for PACS and PBCS dendrimers are shown in Fig. 18. The power M dependences of the dendrimer hydrodynamic radius $R(M)$ may be easily derived from the slopes of the given curves; for PACS [43] the dependence $R(M)$ is characterized by the scaling exponent $\beta = 0.38 \pm 0.02$, and for PBCS the $\beta = 0.34 \pm 0.01$. These β values are very close to the exponents in Eqs. (11a) and (11b).

In several works reporting the study of the symmetrical dendrimer structure [19–21, 25, 50], it was shown that the correlation between the dendrimer sizes and the molecular weight may be described by the empirical relation through the dendrimer generation number, G:

$$R \propto G. \tag{8}$$

A series of M dependences of the dendrimer size are presented in Fig. 19 for polycarbosilane dendrimers. The following curves correspond to PACS dendrimers: curve 1a has been plotted according Eq. (7a), curve 2a according to data from Table 1 and Eq. (8); the dependence of the type $R(M) \propto M^{0.5}$ (the same one as for a linear macromolecule in the Θ solvent) has been calculated with M data of PACS dendrimers (curve 3a) and dependence $R(M) \propto M^{1/3}$, which is expected for identical rigid spheres (curve 4a), are also plotted in Fig. 19. Analo-

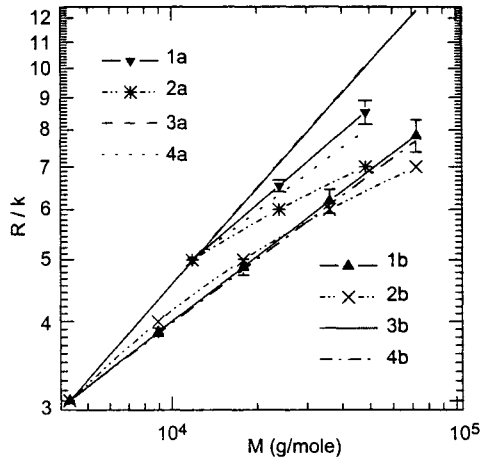

Fig. 19. M dependences of macromolecular size of PACS dendrimers, $R(M) \propto M^{0.39}$ (curve 1a), and PBCS dendrimers, $R(M) \propto M^{0.34}$ (curve 1b), in solutions with deuterated chloroform; the size of the molecules is conventionally presented in the units of the dendrimer generation. Here the M dependences of the sizes of PACS (curve 2a) and PBCS (curve 2b) have been plotted according to Eq. (12) and Table 1, the M dependences of the macromolecular size, $R(M) \propto M^{0.5}$, correspond to the Θ solution of the flexible-chain linear polymer (curve 3a is plotted according to the molecular-weight values of PACS, curve 3b according M of PBCS), and the M dependences of a rigid particle size, $R(M) \propto M^{1/3}$ (curve 4a plotted according to the molecular-weight values of PACS, curve 4b according to M of PBCS) are shown as well. In order to superpose the initial points of all these curves, the M dependences presented have been reduced by a coefficient k equal to 7.06, 5.73, 21.75, 21.86, 4.56, and 5.42 for curves 1a, 1b, 3a, 3b, 4a, and 4b, respectively.

gous dependences are given for PBCS dendrimers: curve 1b has been plotted according to Eq. (7b), the curve 2b illustrates the regularity Eq. (8), the dependence $R(M) \propto M^{0.5}$ plotted as the function of the PBCS molecular-weight data is presented by curve 3b, and the relation $R(M) \propto M^{1/3}$ by curve 4b.

It may be conventionally assumed that curves shown in Fig. 19 characterize three types of macromolecules, which principally differ by the type of dependences $R(M)$. The lines with the slope $\beta = 1/3$ correspond to the macromolecules of the first type. The monomer unit density of these molecules does not depend on their M. The curves with $\beta > 1/3$ and $\beta < 1/3$ characterize macromolecules of the second and third types, respectively; for the molecules of the second type the monomer unit density grows as the M increases, and for the molecules of the third type the given density decreases. Thus, this differentiation of the M dependence curves permits one to state that relation Eq. (8) consistent with the initial theoretical ideas about the structure of the high-generation symmetrical dendrimers (with $G > 5$), assumes an increase of the monomer unit density of dendrimers as their molecular weight increases ($\beta < 1/3$, curves 2a, 2b). In particular, the considerable growth of the monomer unit density inside the dendrimer cell at approaching the limit (critical) generation is expected [4–6], when the following step of the macromolecular synthesis in the ideal branching scheme is impos-

sible. In accord with our experimental data the dependences $R(M)$ corresponding to the polycarbosilane dendrimers ($G = 3$–7) are characterized by the slope $\beta > 1/3$. Consequently, PACS and PBCS dendrimers should be specified as macromolecules of the second type with their own monomer unit density in a solvent decreasing, as the molecular weight of polymeric cell increases. This fact proves the swelling of dendrimers in solutions. It should be noted that the β exponents obtained for PACS and PBCS dendrimers differ. For PACS the value of β is somewhat higher than that for PBCS dendrimers. It means that the density of the PBCS dendrimer having the tetra-functionality core is higher than the density of a PACS dendrimer of the same generation but with a tri-functionality core at otherwise identical conditions (in particular, at the values of the macromolecular radius close enough, see Fig. 18). This result is in accord with common ideas about the dendrimer structure: if the length of the repeat units is the same in the macromolecules of the same generation, then their total number inside the dendrimer cell is the higher, the higher the functionality of the core.

The value of $\beta = 0.34 \pm 0.01$ obtained for PBCS practically coincides with the exponent 1/3 corresponding to the rigid spheres. Nevertheless, it is not correct to reckon the PBCS dendrimers as the absolutely rigid particles, as it was made, for instance, in refs 19 and 28, due to the existence of evident M dependence of the critical concentration, $\hat{\varphi}(M) \propto M^{-0.104 \pm 0.005}$, obtained for dendrimers of the given family. Thus, in accord with our data the dependence $\hat{\varphi}(M)$ seems as the more sensitive characterization in comparison with $R(M)$, when analyzing the changes of the dendrimer microscopic structure and, in particular, the features of changes of the monomer unit density as the dendrimer M increases.

4 Conclusions

PFG NMR and the use of a high enough PFG amplitude permitted us to study the self-diffusion of dendrimers in solutions over the wide range of molecular weights and macromolecular concentrations. The generalized concentration dependence of the normalized diffusion rates of dendrimers was obtained as a function of the relative concentration $\varphi/\hat{\varphi}$ when experimental data were analyzed. This result permits us to talk about general regularities of dendrimer translational mobility in solutions, at least for dendrimers of the studied families (PACS, PBCS and PAMAM-OH). It was also shown that individual features of the dendritic matrix structure, the chemical nature of its structural units, the content and temperature of solutions do not considerable affect the shape of the generalized concentration dependence of the dendrimer diffusion rates D'.

For the first time, the molecular-mass dependences of the critical concentration $\hat{\varphi}(M) \propto M^{-0.18 \pm 0.01}$ and $\hat{\varphi}(M) \propto M^{-0.104 \pm 0.005}$ were obtained for macromolecular solutions. The assumption about the functional correlation between the M dependences for the critical concentrations and for macromolecular size $R(M)$ was made within the frames of the dynamic scaling theory and was proved by good coincidence of the experimental and the calculated curves for the dendrimer size

obtained. The analysis of the dependences $\hat{\varphi}(M)$ permitted us to make a qualitative conclusion about the changes of the own monomer unit density depending on the dendrimer generation, i.e., to characterize the features of macromolecular structure.

Acknowledgements

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