Generalized Concentration Dependence of Self-Diffusion Coefficients in Poly(allylcarbosilane) Dendrimer Solutions

A. I. Sagidullin,*,† A. M. Muzafarov,‡ M. A. Krykin,‡ A. N. Ozerin,‡ V. D. Skirda,† and G. M. Ignat'eva‡

Department of Molecular Physics, Kazan State University, Kremlevskaya Str., 18; 420008 Kazan, Russia, and Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Sciences, Profsoyuznaya Str., 70; 117393 Moscow, Russia

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ABSTRACT: Self-diffusion of three high generations (the fifth, sixth, and seventh) of poly(allylcarbosilane) dendrimer in solutions with deuterated chloroform has been studied over a wide range of macromolecular concentrations (φ). Diffusivity has been measured by NMR with a pulsed gradient of the magnetic field. It is shown that concentration dependences of the dendrimer self-diffusion coefficients (D) can be reduced to the generalized concentration dependence. Over the range of volume concentrations from 0.01 up to 0.55, the curve of the generalized dependence of D for dendrimers coincides with the analogous dependence for globular protein in aqueous solutions. Analogous to the universal concentration dependence of D for linear polymers in solvent, the generalized concentration dependence of dendrimers tends to the asymptote $D'(\varphi)/D_0 \propto \varphi^0 = 1$ in the limit of extremely dilute solutions and to the asymptote $D'(\varphi)/D_0 \propto \varphi^{-3}$ in the range of concentrated solutions $0.3 < \varphi < 0.55$. Here, $D_0 = \lim_{\varphi \to 0} D(\varphi)$ and $D(\varphi)$ are the self-diffusion coefficients of dendrimer in an extremely dilute solution and in a solution with macromolecular concentration φ, respectively. $D'(\varphi) = D(\varphi)/L(\varphi)$, where $L(\varphi)$ is a normalizing function, taking into account the change of the local mobility of dendritic branches as the macromolecular concentration increases; the $L(\varphi)$ functions have been experimentally extracted from the concentration dependence of the longitudinal relaxation times for the dendrimers in solutions studied.

Introduction

The interest in research of regular hyperbranched macromolecules (dendrimers[1]) has permanently grown in recent years.[2−5] The chemical[1,5,6] and physical[5,7−10] properties of the dendritic macromolecules are actively studied; such investigations both increase the knowledge about the dendrimers as a novel class of macromolecular substances and facilitate the exact determination of specific fields of their application in chemistry, medicine, pharmacology, etc.[5] In particular, to organize technological processes of dendrimer synthesis and reprocessing, the same as in the case of linear polymers, it is necessary to have precise information about the translational mobility of dendrimers in various solutions and blends. However, self-diffusion of dendritic macromolecules in solutions has been studied by few researchers.[11−13]

Ihre et al.[11] and Gorman et al.[12] studied self-diffusion of dendrimers in dilute solutions by pulsed-field gradient NMR (PFG NMR). Namely, Ihre et al.[11] used NMR equipment with the maximal amplitude of the magnetic field gradient of $g_{max} = 0.07$ T m^{-1}, and Gorman et al.[12] used a bit higher amplitude of pulsed gradient of $g_{max} = 0.53$ T m^{-1}. The values of self-diffusion coefficients (D) of dendrimers were measured, and their hydrodynamic radii were calculated through the Stokes−Einstein formula. The experimental data for dendrimers in deuterated solvent[11] showed that the diffusion decay of the spin-echo signal had an exponential shape. It refers to macromolecules with a sufficiently narrow molecular mass distribution, and this system could be described as a single-component one with respect to NMR diffusometry.[14,15]

A more complete and detailed examination of dendrimer translational mobility was carried out by Rietveld et al.[13] The self-diffusion of poly(propyleneimine) dendrimers was studied in the methanol solutions over the wide range of macromolecular concentrations. The dendrimer D values were measured by the proton PFG NMR with a three-pulse sequence of stimulated spin echo;[16] the maximal amplitude of the magnetic field gradient was $g_{max} = 4.3$ T m^{-1}. For five low generations of the dendritic molecules, the concentration dependences of D were obtained. Rietveld et al.[13] conventionally distinguished three concentration regimes to characterize translational mobility of macromolecules: the regime of dilute solutions (here the volume fraction of dendrimer φ was up to 0.2), the regime of semidilute ($0.2 \le \varphi < 0.4$), and concentrated ($\varphi \ge 0.4$) solutions. In the regime of the dilute solution, the concentration dependence of D was satisfactorily described as follows:

$$D(\varphi) = D_0(1 + k\varphi) \tag{1}$$

where $D_0 = \lim_{\varphi \to 0} D(\varphi)$, D_0 is the self-diffusion coefficient of macromolecules in an extremely dilute solution, and k is a temperature-dependent coefficient.

For semidilute solutions with the dendrimer content $\varphi \ge 0.2$, the concentration dependence was described by an equation deduced within the frame of the free volume theory of Vrentas−Duda:

$$D(\varphi) = D_0 \exp(-\zeta\varphi/(1 - \varphi)) \tag{2}$$

where ζ is the overlap factor and $(1 - \varphi)$ is the free volume taken by methanol. According to ref 13, the

† Kazan State University.
‡ Russian Academy of Sciences.
* To whom correspondence should be addressed: e-mail Alexandr.Sagidullin@ksu.ru; Tel 007-8432-315189.

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interactions between dendrimers considerably influence the molecular motion in semidilute solutions. For macromolecules of the fourth and fifth generations, the concentrated regime of self-diffusion was found in solutions with the dendrimer content $\varphi > 0.4$. However, the concentration dependences of D were not satisfactorily described by the free volume theory. The last diffusion regime was not observed for three lower generations of the poly(propyleneimine) dendrimer. Thus, the diffusion behavior of macromolecules in dilute and semidilute solutions was successfully explained within the free volume theory, but Rietveld et al.[13] did not propose any theoretical concept to describe the features of translational mobility of dendrimers in the concentrated regime.

It should be noted that self-diffusion of only low-generation dendrimers (usually up to the fourth or fifth generation[1,5]) was studied in the papers discussed above.[11−13] The translational mobility of high-generation dendrimers has not been studied; nevertheless, it is known[1,5] that the physical and structural properties of the high-generation molecules appreciably differ from the properties and structure of low-generation dendrimers. Only Rietveld et al.[13] reported measurements of macromolecular self-diffusion over the *whole* range of dendrimer concentrations. However, for poly(propyleneimine) dendrimers of the fourth and fifth generations in concentrated solutions the authors did not succeed to explain the character of concentration dependences of D by the free volume theory. In this connection, it is necessary to note that this theory does not allow one to completely describe the diffusion behavior of linear polymers in the regime of the concentrated solution as well. This problem is solved[14,15] more successfully within the frame of de Gennes' dynamic scaling theory[17] than by the free volume theory. In accord with the de Gennes' theory, the concentration dependence of the macromolecular D is described by a general power relation:

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

where the exponent $\alpha(\varphi)$ is a function of the polymer concentration in solution. This dependence tends to characteristic limits, asymptotes, in the range of dilute and concentrated solutions. The asymptotes are mathematically described by eq 3 with the exponent $\alpha = 0$ for the asymptote in the limit of the extremely dilute solutions ($\varphi \to 0$) and with $\alpha = 3$ for the asymptote in range of the concentrated polymer solutions (for $\varphi > \varphi'^*$, where φ'^* is the concentration at which the solution of macromolecules is an entangled polymer system[14,15]).

The practical applicability of the dynamic scaling theory[17] was confirmed by the universal concentration dependence of D, which was experimentally obtained for macromolecules in the linear polymer solutions.[18] This dependence tends to two asymptotes predicted within the de Gennes' theory[17] and formally determined by eq 3 with $\alpha = 0$ at $\varphi \to 0$ and $\alpha = 3$ at $\varphi \to 1$.[14,15,18,19] It should be noted that the universal dependence was derived only after the normalization of experimental concentration dependences of the polymer self-diffusion coefficients by a function $L(\varphi)$. The L function includes information about the dependence of macromolecular local dynamic properties on the polymer concentration,[14,15] and the normalizing procedure with the use of L function was developed and executed to eliminate the influence of the polymeric chain dynamics on the macromolecular translational mobility from the data analysis. Skirda et al.[18] and Aslanyan et al.[19] obtained the L function for each polymer solution using the experimental concentration dependences of macromolecular longitudinal relaxation times, T_1. The relation $L(\varphi) = T_1(\varphi)/T_1(0)$ was used, where $T_1(\varphi)$ and $T_1(0) = \lim_{\varphi \to 0} T_1(\varphi)$ are the spin−lattice relaxation times of macromolecules in a solution with the polymer concentration φ and in an extremely dilute solution, respectively. The universal concentration dependence of D for polymers in solutions is usually plotted in the coordinate frame $\log(D'(\varphi)/D_0)$ vs $\log(\varphi/\hat{\varphi})$, where $D'(\varphi) = D(\varphi)/L(\varphi)$ is the normalized self-diffusion coefficient of macromolecules, $D_0 = \lim_{\varphi \to 0} D(\varphi)$ is diffusivity of polymer in an extremely dilute solution, $L(\varphi)$ is the normalizing function, φ is the volume fraction of macromolecules in solution, and $\hat{\varphi}$ is a critical concentration at which the polymer coils begin to overlap, and as a result, the interactions between the polymer coils substantially influence the macromolecular self-diffusion. The $\hat{\varphi}$ values were experimentally obtained as the crossover of asymptotes $D'(\varphi)/D(0) \propto \varphi^0 = 1$ and $D'(\varphi)/D(0) \propto \varphi^{-3}$. In this manner, on the basis of diffusion measurements, the molecular mass dependence of the polymer critical concentration was defined by the relation[14,15,18,19]

$$\hat{\varphi}(M) \propto M^{-0.50 \pm 0.03} \tag{4}$$

This approach was applicable to polymer solutions with a Θ solvent as well as to solutions with a good solvent.

Nesmelova[20] obtained the generalized concentration dependence of D for globular proteins in aqueous suspensions on the basis of the approach developed in ref 18. The generalized concentration dependence of D for proteins, as well as the analogous dependence for polymers, tends to a constant in the limit of dilute solutions. In the range of concentrated solutions, the generalized concentration dependence of D for proteins is satisfactorily described by eq 3 with $\alpha = 3$. In the intermediate concentration range, the generalized concentration dependence of D for protein essentially differs from the universal dependence for polymers.

The aim of this paper is to study by NMR self-diffusion of three high generations of poly(allylcarbosilane) (PACS) dendrimer ($G = 5-7$) in solutions with deuterated chloroform over the wide range of macromolecular concentrations. It is assumed that dendrimer is a macromolecule composed of monomers (repeated units and terminal groups) like polymer chains. On the basis of this assumption, an attempt of obtaining the generalized concentration dependence of PACS dendrimer self-diffusion coefficients is made by normalization of experimental concentration dependences of macromolecular D, using the $L(\varphi)$ function defined for each dendrimer generation (L functions are obtained by the expression $L(\varphi) = T_1(\varphi)/T_1(0)$, where $T_1(\varphi)$ is the longitudinal relaxation time of dendrimers in the solution with the macromolecular content φ, $T_1(0) = \lim_{\varphi \to 0} T_1(\varphi)$).

Experimental Section

Dendrimers were synthesized in Laboratory of Organosilicon Polymers Molecular Design at the Enikolopov Institute of Synthetic Polymer Materials of RAS (Moscow). Synthesis of similar dendrimers was reported in refs 21 and 22. The sketch of the second-generation molecule ($G = 2$) is depicted in Figure 1 to illustrate the PACS dendrimer structure. As seen in the figure, PACS dendrimer can be characterized as a symmetrical

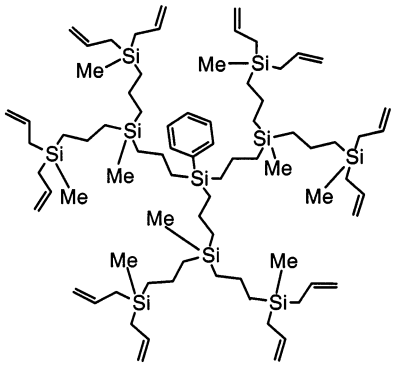

Figure 1. Second-generation molecule of polly(allylcarbosilane) dendrimer, $PhSi_{10}^{12}(All)$. Me is the methyl group.

Table 1. Poly(allylcarbosilane) Dendrimers and Their Solutions with Deuterated Chloroform

generation no.	notation of PACS dendrimers	M_w (g mol^{-1})	range of the dendrimer vol fraction in the solution
5	$PhSi_{94}^{96}(All)$	11 831	0.01−0.57
6	$PhSi_{190}^{192}(All)$	23 952	0.01−0.62
7	$PhSi_{382}^{384}(All)$	48 336	0.01−0.53

cascade hyperbranched macromolecule, a so-called starburst dendrimer.[1] The index of dendrimer polydispersity, M_w/M_n, is about 1.001. Taking into account the possibility of dendrimer cross-links, macromolecules were kept in dilute solutions with deuterated chloroform, with the dendrimer weight concentration of up to 0.09.

The macromolecular content is usually presented by the volume fraction φ. For molecules of PACS dendrimer in solutions, it was calculated as

$$\varphi = \left(1 + \frac{v_s}{v_d}\frac{w_s}{1 - w_s}\right)^{-1} \quad (5)$$

where w_s is the weight fraction of deuterated chloroform in solution; v_d and v_s are the specific volumes of chloroform and dendritic chains, respectively. The following values of specific volumes were used for calculations: $v_s = 0.67$ cm^3 g^{-1} and $v_d = 1.1$ cm^3 g^{-1}. The characteristics of PACS dendrimer macromolecules and their solutions are presented in Table 1.

The self-diffusion coefficient of macromolecules in PACS dendrimer/deuterated chloroform solutions, D, was measured by PFG NMR on a spectrometer operating at the proton resonance frequency 64 MHz. The three-pulse sequence of stimulated spin echo[16] was used. The maximal amplitude of the pulsed field gradient, g_{max}, was 30 T m^{-1}. The time period between the first and second radio-frequency (rf) pulses, τ, was varied from 1.5 up to 4.5 ms, and the duration of the magnetic field pulse, δ, was varied from 0.15 up to 2.5 ms, depending on the experimental conditions. The diffusion observation time,[14,15] $t_d = (\Delta - \delta/3)$, was established in the interval from 7 to 450 ms. (Here Δ is the time period between the pulses of the magnetic field gradient.) The diffusion decays of the stimulated spin-echo signal were registered as the functions of the pulsed gradient amplitude at fixed values of other experimental parameters.

The measurements of spin−lattice relaxation times of dendrimers in solutions, T_1, were carried out with an NMR spectrometer operating at the proton resonance frequency 19.5 MHz. The original sequence of rf pulses was used to measure T_1 values by one scan.[23]

The inaccuracies of measurements of D and T_1 were not higher than 10% at worst. The temperature of measurements was 30 ± 1 °C.

Features of Experimental Methods. In PFG NMR, the initial information about macromolecular self-diffusion is extracted from the diffusion decays (DD) of the spin-echo signal

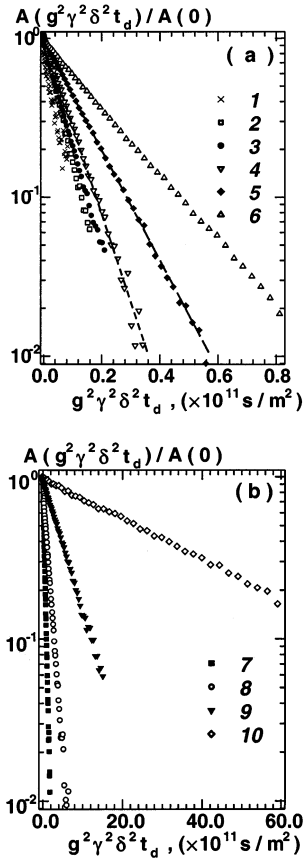

Figure 2. Diffusion decays of the spin-echo amplitude obtained for solutions of the fifth-generation PACS dendrimer with the macromolecular volume fraction: (a) 0.01 (curve 1), 0.05 (curve 2), 0.10 (curve 3), 0.14 (curve 4), 0.21 (curve 5), and 0.27 (curve 6); (b) 0.33 (curve 7), 0.41 (curve 8), 0.49 (curve 9), and 0.51 (curve 10).

amplitude. In the simplest case, when the system is characterized as a single-component one with respect to NMR diffusometry and when the condition $g\delta \gg g_0\tau$ holds (g is the amplitude of the pulsed magnetic field gradient, and g_0 is the steady gradient of a magnetic field), the shape of DD is described by equation[14,15]

$$A(g^2,\tau,\tau_1) = A(0,\tau,\tau_1)\exp(-\gamma^2 g^2 \delta^2 t_d D) \quad (6)$$

where $A(0,\tau,\tau_1)$ is the amplitude of the spin-echo signal at $g = 0$, γ is the proton gyromagnetic ratio, D is the self-diffusion coefficient, and τ_1 is the time interval between the second and third rf pulses of the stimulated spin-echo sequence. It is necessary to note that the magnitude $A(0,\tau,\tau_1)$ includes information about nuclear relaxation in a given system of spins.[14,15] For the systems, whose properties are characterized by diffusion NMR as multicomponent, the DD curve cannot be described by eq 6 due to its complicated shape. In some cases the DD shape depends on the diffusion observation time. Then, analyzing the dependence of the DD shape on the diffusion time, it is possible to determine, for example, if the intermolecular structures (the so-called dynamic clusters) are present in the studying systems and to estimate the lifetimes of these clusters.[14,15,19]

Results and Discussion

DD Shape for PACS Dendrimer/Deuterated Chloroform Solutions. The DDs, which have been obtained for PACS dendrimer of the fifth generation/deuterated chloroform solution, are presented in Figure 2. Their shape is single-exponential; it is described by eq 6 and is characterized by the self-diffusion coefficient, D,

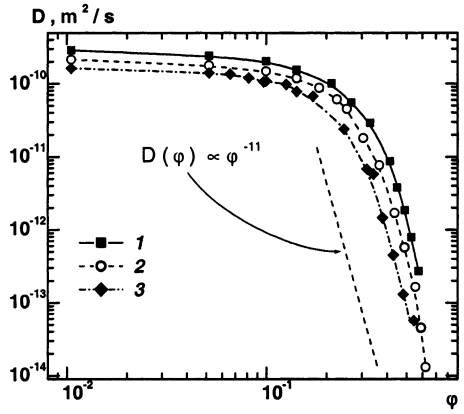

Figure 3. Concentration dependences of the dendrimer self-diffusion coefficient for macromolecules of the fifth (curve 1), sixth (curve 2), and seventh (curve 3) generations.

depending on the macromolecular concentration φ only. The DDs, obtained for dendrimers of the sixth and seventh generations, also have an exponential shape. It has been determined that the DD shape does not depend on the diffusion time, t_d, for all studied dendrimers. Thus, in contrast to the behavior of polymers in solutions, the obtained diffusion decays do not allow us to state that any intermolecular structures are present in PACS dendrimer/deuterated chloroform solutions. The simple single-exponential DD shape is also in accord with to idea that the dendrimer is a system with exceedingly narrow molecular mass distribution.

Concentration Dependences of the Dendrimer Self-Diffusion Coefficients. The concentration dependences of D are depicted in Figure 3 for PACS dendrimer of the fifth, sixth, and seventh generations. In the range of concentrated solutions, the obtained dependences of D on the PACS dendrimer concentration, as well as the dependences of D for the poly(propyleneimine) dendrimers of the fourth and fifth generations in ref 13, could not be described within the free volume theory by means of the relation of the type 2. For PACS dendrimer solutions, the analysis of the DD shape is carried out, using the general statements of the dynamic scaling theory.[14,15,17] To determine the value of the exponent α in eq 3, the concentration dependences of PACS dendrimer D have been plotted in the coordinate frame log $D(\varphi)$ vs log φ (Figure 3). As seen in Figure 3, two characteristic domains can be discriminated in these curves. In the limit of dilute solutions, these dependences are satisfactorily described by eq 3 with $\alpha = 0$ and in the range of concentrated solutions (at $\varphi \rightarrow 0.55$) with the exponent α of about 11.

To reduce the obtained concentration dependences of D to a generalized form and hereafter not to consider the influence of the local dynamics of dendritic cell on the dendrimer self-diffusion, the dependences have been normalized by the L function, corresponding to each macromolecular generation. The values of the dendrimer self-diffusion coefficient in an extremely dilute solution, D_0, have been determined by a linear extrapolation of dependences $D(\varphi)$ to the zero concentration of dendrimer.

Obtaining *L* Functions. Concentration Dependences of Longitudinal NM Relaxation Times. To define the normalizing L functions for PACS dendrimers of the fifth, sixth, and seventh generations, the spin−lattice relaxation times, T_1, have been measured. The

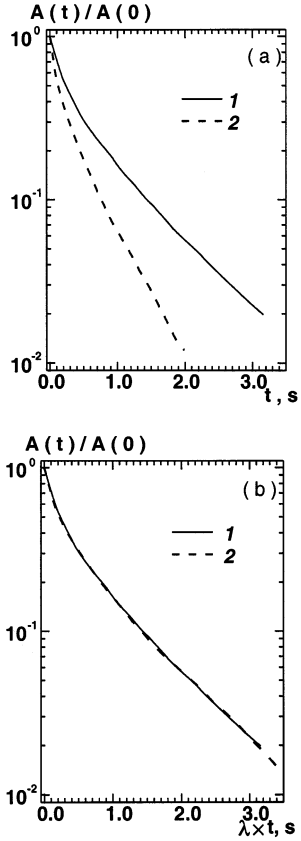

Figure 4. (a) T_1 relaxation attenuations of magnetization for the sixth-generation dendrimer in deuterated chloroform solutions with the dendrimer volume fraction: 0.23 (curve 1) and 0.44 (curve 2). (b) The same attenuations but plotted in the coordinate frame with the scaled abscissa axis; the scaling coefficient, λ, is 1 for the curve corresponding to the solvent with $\varphi = 0.23$, and $\lambda = 2.7$ for the solution with $\varphi = 0.44$.

typical T_1 relaxation attenuations of magnetization for the examined dendrimers are presented in Figure 4a. As seen in the figure, the curves have a complicated nonexponential shape, and they are characterized by a spectrum of T_1 times. This spectrum may be explained by both the presence of nonequivalent protons in the methyl, methylene, and allyl groups of the dendrimer structure and the possible difference of branch mobility depending on its remoteness from dendrimer core. The verification of the latter hypothesis is related to present-day problems in studying the branch local mobility inside the dendritic cell. However, their solution is connected with a necessity to synthesize special molecules with selective substitution (deuteration) of dendrimer cascades.

Let us come back to the challenge of obtaining the normalizing functions. In refs 18−20, the procedure of the L function determination was sufficiently easy inasmuch as generally the single T_1 characterized the spin−lattice relaxation. In our case, obtaining L functions becomes problematical due to the uncertainty in choosing the necessary T_1 component of the spectrum. This problem could be appreciably simplified, if all the T_{1i} values in the spectrum varied equally with the increase of the macromolecular concentration in solution or, in other words, if the symbate change of all components in the T_1 spectrum existed. In that case, to obtain the L function, using the relation $L(\varphi) = T_1(\varphi)/T_1(0)$, it is possible to use an arbitrary T_{1i} from the spectrum. In Figure 4b, it is visually demonstrated that the

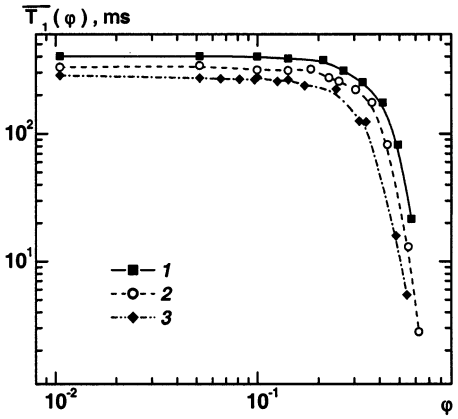

Figure 5. Concentration dependences of the mean spin−lattice relaxation times for the dendrimer of the fifth (curve 1), sixth (curve 2), and seventh (curve 3) generations in solutions.

symbate decrease of all components of the T_1 spectrum actually exists. In this figure, the same relaxation attenuations, as in Figure 4a, are shown, but in the coordinate frame $\log(A(t)/A(0))$ vs $\log(\lambda t)$, with the scaled abscissa axis; here λ is a scaling coefficient. It equals 1 for the curve 1, and the curve 2, λ is fitted according to condition of the best coincidence of these two curves in the scaled coordinates, and it equals 2.7. Here the scaling procedure is applied to the abscissa axis to analyze the relaxation attenuation curves and to reveal the features of the variations of the T_{1i} components from the spectrum as the dendrimer concentration increases in solution. In the result of scaling, as seen in Figure 4b, the curves completely coincided, proving the symbate change of all T_{1i} values from the spectrum for dendrimers, depending on concentration. In our case this result has the following formal description: $T_{11}(0.23) = \lambda T_{11}(0.44)$, $T_{12}(0.23) = \lambda T_{12}(0.44)$, ..., $T_{1i}(0.23) = \lambda T_{1i}(0.44)$, and so on ($i = 1, 2, ...$), where $T_{1i}(0.23)$ and $T_{1i}(0.44)$ are the ith component from the longitudinal relaxation times spectrum of dendrimer in solution with $\varphi = 0.23$ and $\varphi = 0.44$, respectively.

Thus, to define L functions, it is possible to use arbitrary T_{1i} values from the spectrum, including the corresponding mean spin−lattice relaxation time, $\bar{T}_1$. The use of $\bar{T}_1$ is more correct than the use of any other T_{1i} value from the spectrum inasmuch as $\bar{T}_1$ characterizes the total spectrum (in accord with the definition $1/\bar{T}_1 = \sum_i p_i/T_{1i}$, where T_{1i} is the ith component of the spectrum and p_i is the relative population of spins for a given component), and, moreover, $\bar{T}_1$ can be always extracted from the initial slope of the relaxation attenuation curve.

Finally, the normalizing functions were extracted from experimental concentration dependences of times $\bar{T}_1(\varphi)$ (see Figure 5) through the expression

$$L(\varphi) = \frac{\bar{T}_1(\varphi)}{\bar{T}_1(0)} \tag{7}$$

where $\bar{T}_1(\varphi)$ and $\bar{T}_1(0)$ are respectively the mean value of the spin−lattice relaxation time for dendrimer in a solution with macromolecular content φ and that in the limit of an extremely dilute solution. The value $\bar{T}_1(0)$ was defined by a linear extrapolation of the corresponding dependence $\bar{T}_1(\varphi)$ to the zero concentration.

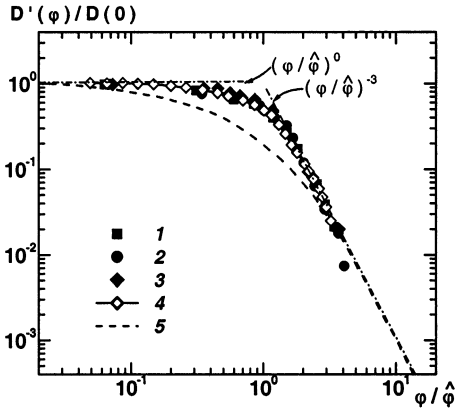

Figure 6. Concentration dependences of D for the dendrimer of the fifth (curve 1), sixth (curve 2), and seventh (curve 3) generations in solutions with deuterated chloroform obtained by the normalization of experimental dependences of the dendrimer self-diffusion coefficient with an $L(\varphi)$ function corresponding to each generation. The generalized concentration dependence of D for globular proteins in aqueous suspensions (curve 4) and the universal concentration dependence of D for linear polymers in solutions and melts (curve 5) have been also shown. The characteristic asymptotes, $D'(\varphi)/D_0 \propto (\varphi/\hat{\varphi})^0$ and $D'(\varphi)/D_0 \propto (\varphi/\hat{\varphi})^{-3}$, are denoted by dashed−dotted lines.

Generalized Concentration Dependence of *D* for PACS Dendrimers. After the normalization of experimental concentration dependences of dendrimer D by an L function, corresponding to each generation, three similar curves characterized by two asymptotes were obtained in the coordinate frame $\log(D'(\varphi)/D_0)$ vs $\log \varphi$. The form of the asymptotes is formally determined by eq 3 with $\alpha = 0$ in the limit of extremely dilute solutions and with $\alpha = 3$ in the range of concentrated solutions (at $\varphi \rightarrow 0.55$). The values of the critical concentration $\hat{\varphi}$ were extracted from the crossover of the asymptotes. The sufficient arguments to apply this simple method to determine $\hat{\varphi}$ were the similarity of the obtained curves and the necessity to define the dependence $\hat{\varphi}(M)$ and not absolute values of the critical concentration. The $\hat{\varphi}$ values obtained in this way were 0.17 ± 0.01, 0.15 ± 0.01, and 0.14 ± 0.01 for dendrimers of the fifth, sixth, and seventh generations, respectively. As a result, the molecular mass (M) dependence of the critical concentration for PACS dendrimers is satisfactorily described by the empirical relation

$$\hat{\varphi}(M) \propto M^{-0.18\pm0.01} \tag{8}$$

The concentration dependences of D for the dendrimers of the fifth, sixth, and seventh generations are depicted in Figure 6 in coordinates $\log(D'(\varphi)/D_0)$ vs $\log(\varphi/\hat{\varphi})$. In this coordinate frame, all three curves are united into the generalized concentration dependence of D for PACS dendrimers. This dependence allows us to discuss common regularities of PACS dendrimer diffusion in solutions with deuterated chloroform, at least, for macromolecules of three high generations.

The universal concentration dependence of D for macromolecules in linear polymer solutions,[14,15,18,19] and the generalized concentration dependence of D for globular proteins in aqueous suspensions[20] are shown in Figure 6 for comparison. As seen in this figure, the obtained concentration dependence of dendrimer D coincides with the universal dependence for linear polymer only in the limit of dilute solutions and in the

range of concentrated solutions. In the intermediate range of the macromolecular concentration, these two curves differ. This result indicates appreciable distinctions in the diffusion behavior of dendrimers and linear polymers. In the given concentration range, the dynamic intermolecular interactions begin to dominantly influence macromolecular translational mobility.[14,15] Usually, the mechanisms and character of these interactions depend on structural features of polymeric chains.[14,17,20] Consequently, the differences between the generalized concentration dependence of D for dendrimers and the universal dependence for linear polymers (see Figure 6) might be due to the non-Gaussian conformation of the dendritic macromolecule[1−5] and, as a result, to specific mechanisms of the intermolecular interaction, differing from those in polymers. Another type of macromolecules, whose conformation appreciably differs from linear polymer coils, is globular protein. The differences in the diffusion behavior of proteins and linear polymers were explained by the rigid globular structure of the peptide chain[20] and, as a consequence, by the features of the intermolecular protein interaction different from those for polymer. Comparing the generalized concentration dependence of peptide D (curve 4) and the universal dependence for polymers (curve 5) in Figure 6, this difference can be easily observed. At the same time, the comparison of the generalized concentration dependence of protein D with the same curve for dendrimers shows that they coincide over the whole examined range of the macromolecular concentration. This result allows us to characterize the behavior of dendritic macromolecules as systems having mechanisms of the intermolecular interaction similar to those in globular proteins. The absence of entanglements and sufficient penetrations of macromolecules is apparently the dominant factor of the interaction both for dendrimers and proteins. Moreover, the evident differences of the structure and the extent of the intramolecular interaction for proteins and nonpolar carbosilanes do not practically influence the macromolecular mobility in the studied solutions.

Let us turn to discussing the M dependence of the critical concentration $\hat{\varphi}$ for the dendrimers (eq 8). It is well-known that for the suspension of equal rigid spheres the value of the overlap concentration does not depend on the particle M. In the case of a linear polymer coil solution,[14,15,18] the dependence of the coil overlap concentration, $\hat{\varphi}$, on the polymer chain molecular mass is determined by eq 4. Furthermore, for polymer solutions with a Θ solvent, it was established that the experimental dependence $\hat{\varphi}(M)$ coincides with the M dependence of the coil overlap, $\varphi^* \propto M/R^3(M)$, predicted by the dynamic scaling theory;[14,17] here R is the Flory radius with a power-scaling M dependence $R(M) \propto M^{\beta}$. Usually β varies from 0.5 up to 0.6 depending on the solvent quality. If, in the case of dendrimers, $\hat{\varphi}$ is the concentration of the dendritic sphere overlap, then it is possible to obtain the M dependence of the dendrimer size. If it is assumed that the relation $R(M)$ for dendrimers is described by a scaling law, $R(M) \propto M^{\beta}$, and that the M dependence of $\hat{\varphi}$ for dendrimer/solvent systems is connected with $R(M)$ in the same way as the overlap concentration, $\varphi^* \propto M/R^3(M)$, then, using eq 8, the following is derived:

$$M/R^3(M) \propto M^{-0.18\pm0.01} \tag{9}$$

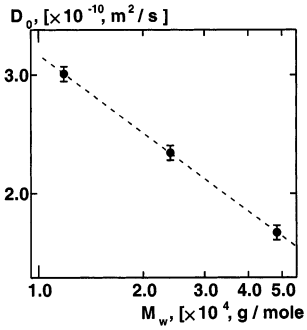

Figure 7. M dependence of self-diffusion coefficients D_0 for a PACS dendrimer in an extremely dilute solution.

Thus, within the limits of our arguments, the M dependence of the PACS dendrimer size is described by a scaling relation:

$$R(M) \propto M^{0.39\pm0.02} \tag{10}$$

As the relation 10 shows, the value of the M exponent is substantially smaller than the values 0.5−0.6 appropriate for linear polymers. It is necessary to note that the dependence $R(M)$ can be obtained by the traditional method, the calculation of the macromolecular hydrodynamic radius by the Stokes−Einstein formula[11−13,24] and using the value of the dendrimer self-diffusion coefficient in an extremely dilute solution, D_0. The M dependences of D_0 are presented in Figure 7. With these dependences, it is easy to obtain the scaling dependence of the dendrimer hydrodynamic radius, $R(M)$, with M exponent $\beta = 0.38 \pm 0.02$. This β value is close to the exponent 0.39 ± 0.02 in eq 10.

It is interesting to compare the obtained eq 10 for the PACS dendrimers with the known regularities for other types of macromolecules (linear polymers, rigid particles) and with the empirical relation[1,5,11] establishing the correlation between the size of dendrimer and its M via the generation number, G:

$$R \propto G \tag{11}$$

The M dependences of the PACS dendrimer size are presented in Figure 8: curve 1 has been plotted by eq 10, and curve 4 by relation 11 with the data from Table 1. The dependence $R(M) \propto M^{0.5}$ for linear polymer in a Θ solvent (curve 2) and the dependence $R(M) \propto M^{1/3}$(curve 3) expected for equal rigid spheres are also shown in this figure. It may be arbitrarily determined that curves in Figure 8 characterize three types of molecules. The line with the slope $\beta = {}^1/_3$ describes the first type of molecules, and the monomer unit density for these molecules does not depend on M. The curves with $\beta > {}^1/_3$ and $\beta < {}^1/_3$ characterize respectively the second and the third types of macromolecules. This differentiation allows us to state that as M increases, the own monomer unit density decreases for the second type macromolecules, but it increases for the third type molecules. As seen in Figure 8, eq 11 predicts the increase of the own monomer unit density as the dendrimer M increases. It is expected for symmetrical macromolecules of high generations ($G > 5$) in accord with theoretical ideas about the structure of starburst[1] dendrimers. In particular, the essential increase of the own monomer unit density in the dendrimer cell is foreseen at the approach to the limit generation.[1,4−6] This makes synthesis of the following dendrimer gen-

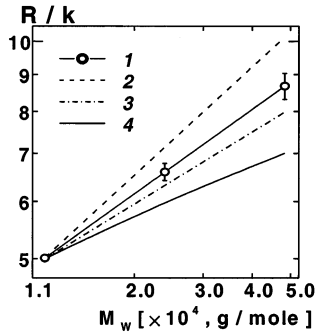

Figure 8. *M* dependence of the macromolecular size for the PACS dendrimer/deuterated chloroform solutions, $R(M) \propto M^{0.39}$ (curve 1); the size of a molecule is conventionally presented in the units of the dendrimer generation number. Here the *M* dependence of the macromolecular size, $R(M) \propto M^{0.5}$, in a Θ solution of a flexible-chain linear polymer (curve 2); the *M* dependence of a rigid particle size, $R(M) \propto M^{1/3}$(curve 3), and the *M* dependence of the size of PACS dendrimers (curve 4) plotted in accord with eq 11 and data from Table 1 are shown as well. To superpose the initial points of these curves, the *M* dependences have been reduced by a coefficient *k* equal to 7.74, 21.68, and 4.56 for curves 1, 2, and 3, respectively.

eration without defects of branching impossible. In accord with our experimental data, it is necessary to relate the examined PACS dendrimer to macromolecules of the second type, i.e., to macromolecules whose own monomer units density decreases as its *M* increases. This fact indirectly evidences the dendrimer swelling although in an essentially smaller extent if compared with the linear polymer coils. This result is rather unexpected because it has been supposed that the seventh generation of PACS dendrimer is limit, and the following synthesis of the dendrimer is impossible without defects of branching regularity.

As shown in a series of reports,[13,24] studying the *M* dependence of the low-generation dendrimer size led to scaling relations between the dendrimer radius and the dendrimer molecular weights with the *M* exponent β from 0.36 up to 0.40. In accord with ideas about the cell structure of low-generation dendritic macromolecules,[1,5] our result is entirely predictable, if one assumes that the seventh generation of PACS dendrimer is not yet the limit.

In addition to that said above, it is necessary to note that the existence of the *M* dependence of the dendrimer critical concentration $\hat{\varphi}$ (eq 8) itself infers a more careful attitude to the modeling of high-generation dendrimers by the absolutely rigid particles. At the same time, the terms "flexibility of dendrimer" and "the dendrimer swelling" need a more precise definition by various techniques and, what is not of less importance, with a homologous series of dendrimers with different chemical nature.

Conclusions

The experimental concentration dependences of *D* for high-generation PACS dendrimers can be unified in the generalized concentration dependence of *D*, indicating the existence of common regularities of PACS dendrimer translational mobility. Over the whole range of the studied concentrations of dendrimers in solutions, the generalized concentration dependence of dendrimer *D* coincides with the analogous concentration dependence of protein *D* in aqueous suspensions.[20]

For a macromolecule/solvent system, the *M* dependence of a critical concentration, $\hat{\varphi}(M) \propto M^{-0.18\pm0.01}$, has been derived for the first time when obtaining the generalized concentration dependence of dendrimers *D*. The conclusion about the correlation between $\hat{\varphi}(M)$ and the molecular-mass dependence of the dendrimer size has been made on the basis of the dynamic scaling theory,[17] conclusions from ref 18, and results of our study. The analysis of $\hat{\varphi}(M)$ led to an unexpected result: the own monomer unit density in a cell of the high-generation PACS dendrimers decreases with the growth of dendrimer molecular mass, although it should increase in accord with theoretical ideas about the cell structure for a high-generation dendrimer.[1,5] Furthermore, this result enables a new critical consideration of the notion of the dendrimer limit generation.[1]

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