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Molecular characteristics of poly(propylene imine) dendrimers as studied with translational diffusion and viscometry

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Abstract The generation of dendrimers based on poly(propylene imine) with CN end groups [DAB–dend–(CN)$_x$] and with palmitoyl end groups [DAB–dend–(C15)$_x$] was studied by methods of translational diffusion and viscometry. The volumes of the DAB–dend–(CN)$_x$ and DAB–dend–(C15)$_x$ dendrimers and the previously studied DAB–dend–(lacto)$_x$ dendrimer were compared to evaluate the volumes of the end groups in hybrid dendrimers. The volume of the hybrid dendrimers compared to that of the initial dendrimers increases proportionally to the number of end groups: this means that the end groups are predominantly located on the periphery of each molecule, thus ensuring this volume will increase. It is shown that the volume of the end groups for DAB–dend–(C15)$_x$ is 3.5 times greater, and for DAB–dend–(lacto)$_x$ it is 5.0 times greater than that occupied by free molecules corresponding to the end groups. The values of the intrinsic viscosity were compared with the values of the diffusion coefficient and the chemical formula molecular weight.

Keywords Dendrimers · Hydrodynamic properties · Volume of end groups

Introduction

Dendrimers, which are regularly branched molecules, have become the subject of intensive study. This class of compounds has received increasing attention during the last few years owing to their new chemical fashion and unique physical properties. The interest in these molecules derives from the possibility of using their regular structure in various fields of supramolecular chemistry and molecularly controlled materials technology [1–6].

Dendrimers are very interesting for studies in molecular physics mainly because of their regular branching. A series of dendrimers (assumed to be a homologous series) consists as a rule of five or six generations. The first and second generations belong to the low-molecular-weight region, whereas the fifth and following generations are high-molecular-weight compounds. Thus, the set of experimental data in the case of dendrimers is always limited. The peculiarities of a dendrimer series are the limiting and transitional character of the range of molecular weights. It is noteworthy that in the hierarchy of linear polymers in the transitional oligomer region the greatest changes occur in the many characteristics and/or relationships describing the behaviour of linear molecules [7, 8]. The situation becomes more complex in the study of hybrid dendrimers with end groups, the chemical nature of which differs from that of the core and, possibly, the end groups exhibit additional, specific interactions with this core.

Many reports are available on the synthesis of dendrimers, their chemical modifications, and their computer simulation. Reports studying the molecular properties of dendrimers by different physical techniques are not numerous enough. In general, dendrimer molecules were studied by neutron scattering [9–18], X-ray scattering [10, 19, 20], light scattering [21, 22], and by size-exclusion chromatography [21, 23–26]. In several works the hydrodynamic properties of dendrimer molecules were measured by different techniques [9, 16, 21–39]. It is reported that the intrinsic viscosity of dendrimer molecules is small and has a very low dependency on the molecular weight or that this dependency has a small maximum depending on the number of generations. Small and virtually constant values of the intrinsic viscosity mean that the additional losses for the rotational friction due to the presence of the dendrimer molecules in solution are low. The fact that the $[\eta]$ values of dendrimer molecules are virtually independent of the molecular mass means that the volume of the dendrimer molecules changes practically proportionally to the mass: $V \sim R^3 \sim M$. This allows us to predict that the translational friction coefficient, f, which is proportional to the molecular size, should be more sensitive to the molecular-weight changes on passing from one generation to another because $f \sim R \sim M^{1/3}$. This semiquantitative conclusion was confirmed by the hydrodynamic study of different series of dendrimers [21, 29–32, 34, 37]. In contrast to the value of $[\eta]$, the characteristics related to the translational friction coefficient change considerably and regularly on passing from one generation to another. If the values of the intrinsic viscosity fluctuate about a low mean value, the translational friction coefficient varies regularly and this change is 3–4 times on passing from the first to the sixth generation.

The aim of the present work is to estimate quantitatively the change in the size/volume ratio of dendrimer molecules with different end groups attached to the same core.

Poly(propylene imine) dendrimers are among the best investigated dendrimer systems [40–43]. Using them, numerous hybrid dendrimers have been obtained with various end groups, and these exhibit unique properties [43–46]. In the present work two series of dendrimers based on poly(propylene imine) with CN end groups [DAB–dend–$(CN)_x$] and with palmitoyl end groups [NHCO–$(CH_2)_{15}$–CH_3] [DAB–dend–$(C15)_x$] [47] were studied by the investigation of translational diffusion and the intrinsic viscosity of these molecules. Similar hydrodynamic data obtained previously in the study of lactopoly(propylene imine) dendrimers [DAB–dend–$(\text{lacto})_x$] containing lactose end groups are also discussed [29, 30].

Methods

The initial DAB–dend–$(NH_2)_x$ dendrimers and DAB–dend–$(CN)_x$ generations were obtained by the methods of divergent synthesis as described in Ref. [40]. The core of the of the initial DAB–dend–$(NH_2)_x$ dendrimers represents diaminobutane. Subsequent generations were synthesized by a repeated sequence of the reactions of acrylonitrile addition to primary amines followed by hydrogenation of the nitrile terminal groups. DAB–dend–$(C15)_x$ generations were obtained by the replacement of end groups of primary amines in DAB–dend–$(NH_2)_x$ with palmitoyl groups as described in Ref. [47]. The structural formulae of the fifth generations of the DAB–dend–$(CN)_x$ and DAB–dend–$(C15)_x$ dendrimers are given in Fig. 1).

The translational diffusion properties of dendrimer molecules were studied on a device in which the recording optical system was the Lebedev polarizing interferometer. Tsvetkov's diffusometer has been repeatedly described in the literature [8, 48]. The boundary between the solution and the solvent was formed in a glass cuvette of length 3 cm along the optical path. The rate of layering the heavier solvent under the solution was $(5–7) \times 10^{-3}$ mls^{-1}. Interference curves which were of symmetric character were processed by the method of maximal ordinate, $H_{\max}$, and area, Q, from which the dispersion of the diffusion boundary, σ^2, was calculated:

$$H_{\max} = (Q/a)\Phi\left(a/2^{3/2}\sigma\right),$$

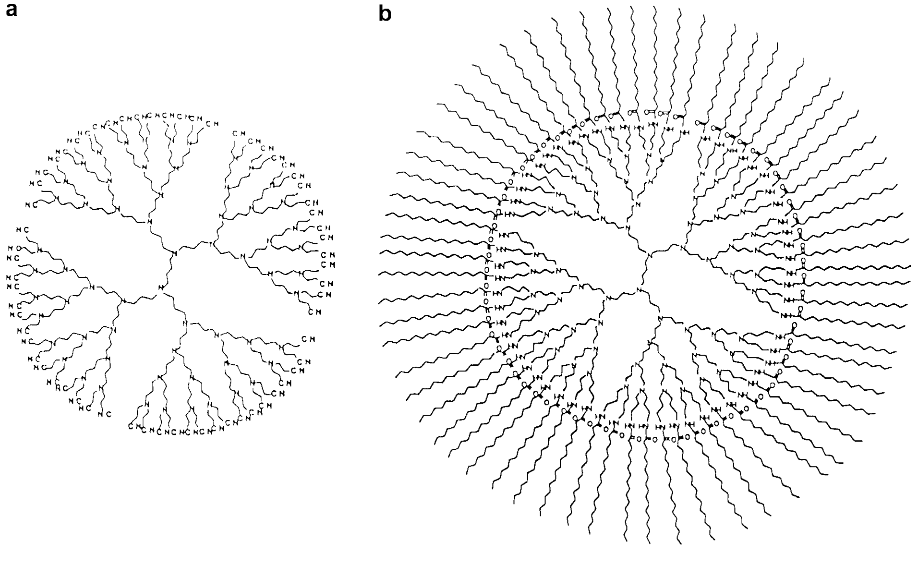

Fig. 1 Two-dimensional structures of fifth generations of **a** DAB–dend–$(CN)_5$ and **b** DAB–dend–$(C15)_5$

where a is the twinning value of Iceland spar plates forming the polarizing interferometer, σ is the standard deviation, and $\Phi(x)$ is the probability integral. The translational diffusion coefficient, D, was determined from the relation $\sigma^2 = \sigma_0^2 + 2Dt$, where σ_0^2 is the initial dispersion characterizing the quality of diffusion boundary formation. The dependence of the dispersion on the diffusion time for five generations of DAB–dend–$(CN)_x$ is shown in Fig. 2. The dendrimer solution concentrations were not above 0.55×10^{-2} gcm^{-3} for DAB–dend–$(CN)_x$ and 0.33×10^{-2} gcm^{-3} for DAB–dend–$(C15)_x$ solutions. So the parameter $c[\eta]$ characterizing the degree of solution dilution was less than 0.02 for both series of dendrimers. The values of D obtained at these conditions were assumed to be the values extrapolated to zero concentration, D_0. The refractive index increment, dn/dc, (Tables 1, 2) was determined from the area spanned by the interference curve at 550 nm. The diffusion experiments were carried out at 26 °C; at this temperature the viscosity of chloroform is 0.535 cP. UV-spectroscopy-grade chloroform was used for all the measurements.

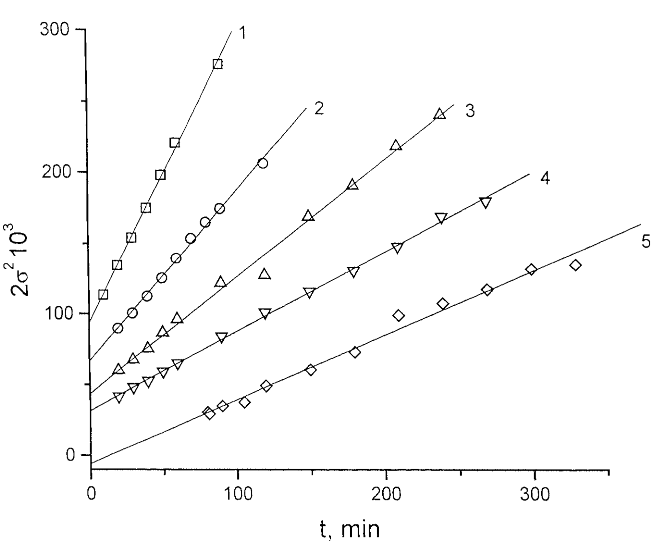

Fig. 2 $2\sigma^2$ (cm^2) versus the time of diffusion, t, for DAB–dend–$(CN)_x$ generations. The *numbers* indicate the number of generations. Each curve is shifted along the $2\sigma^2$ axis by 0.02 cm^2 relative to the previous curve

The intrinsic viscosities of the dendrimers in chloroform, $[\eta]$, and Huggins parameters, k', were determined from the plots $\eta_{sp}/c = [\eta] + k'[\eta]^2 c +$, where $\eta_{sp} = (\eta - \eta_0)/\eta_0$ and η is the viscosity of a solution at a concentration c (Fig. 3). The values of η/η_0 were determined as $\eta/\eta_0 = t/\tau_0$, where t and τ_0 are the times of solution and solvent flow in an Ostwald capillary viscometer.

The experimental results obtained for five generations of DAB–dend–$(CN)_x$ and DAB–dend–$(C15)_x$ are given in Tables 1 and 2.

Discussion

The translational diffusion coefficients decrease markedly and regularly with generation number for the two dendrimer types. In all cases the diffusion coefficients obtained for DAB–dend–$(CN)_x$ exceed those for DAB–dend–$(C15)_x$. The intrinsic viscosities for the dendrimers under investigation are low and in contrast with the diffusion coefficient data do not vary regularly with generation number. It is known [49, 50] that in viscous flow the dissolved molecules are in rotational motion and the intrinsic viscosity is related to the rotational diffusion coefficient, D_r, whereas in the diffusion experiments the translational diffusion coefficients were obtained. The intrinsic viscosities for DAB–dend–$(C15)_x$ slightly exceed those for DAB–dend–$(CN)_x$, on average by 1.5 times. The Huggins parameters are not constant on passing from one generation to another, and the dependence of k' on generation number is of extreme character, differing for different dendrimer types (Fig. 4). The k' values are probably influenced by at least two factors: first, the thermodynamic quality of the solvent and, second, the effects of intramolecular draining. The thermodynamic quality of the solvent may change on passing from one generation to another, and the θ conditions not will be the same for the different generations likes the behaviour of short-

Table 1 Hydrodynamic characteristics of DAB–dend–$(CN)_x$ in chloroform. $r(D)$ and $r([\eta])$ are the linear correlation coefficients of corresponding plots (Figs. 2, 3)

G	$(D \pm \Delta D) \times 10^7$ (cm^{2}s^{-1})	$r(D)$	dn/dc (cm^3/g^{-1})	$([\eta] \pm \Delta[\eta])$ (cm^{3}g^{-1})	$r([\eta])$	k'	M_{theor}
1	85.7 ± 1.5	0.9992	0.079	3.9 ± 0.1	0.9846	0.6	300
2	50.0 ± 1.2	0.9982	0.081	4.6 ± 0.2	0.986	1.25	741
3	34.4 ± 0.4	0.9994	0.086	4.5 ± 0.05	0.999	2.1	1,622
4	23.3 ± 0.3	0.9993	0.083	3.8 ± 0.07	0.999	4.2	3,385
5	19.8 ± 0.6	0.9962	0.083	4.4 ± 0.2	0.9987	3.75	6,910

Table 2 Hydrodynamic characteristics of DAB–dend–$(C15)_x$ in chloroform

G	$(D \pm \Delta D) \times 10^7$ (cm^{2}s^{-1})	$r(D)$	dn/dc (cm^{3}g^{-1})	$([\eta] \pm \Delta[\eta])$ (cm^{3}g^{-1})	$r([\eta])$	k'	M_{theor}
1	49.3 ± 2.2	0.9908	0.046	–		–	1,325
2	29.1 ± 0.7	0.9978	0.040	5.0 ± 0.3	0.9875	1.6	2,789
3	23.8 ± 0.8	0.9952	0.055	6.9 ± 0.3	0.9689	0.44	5,719
4	20.8 ± 1.9	0.9766	0.053	6.2 ± 0.1	0.9978	0.41	11,578
5	16.7 ± 0.7	0.9954	0.059	7.1 ± 0.7	0.9367	0.91	23,296

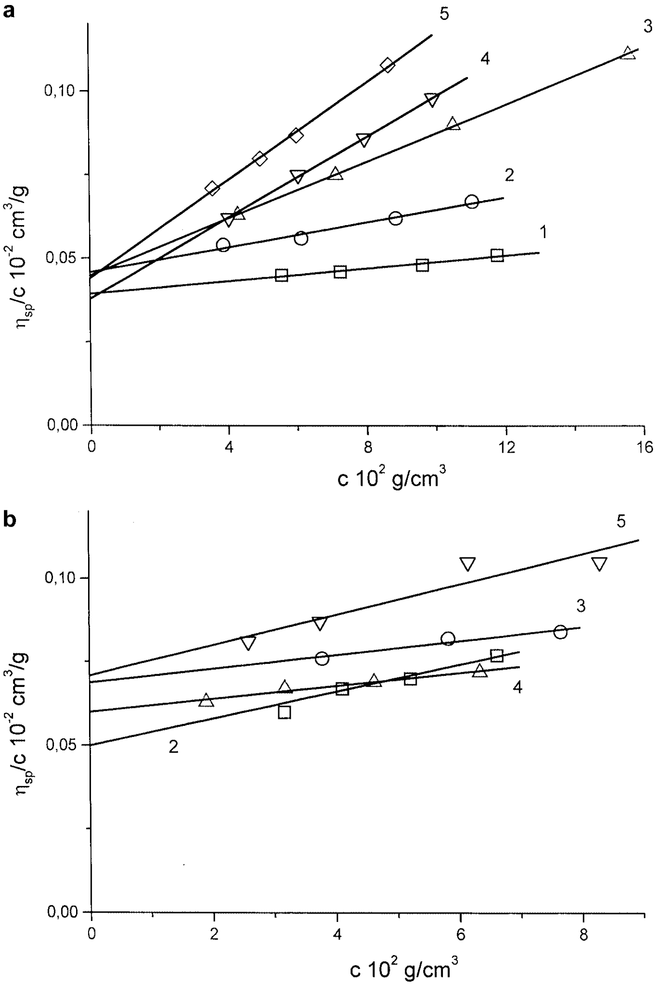

Fig. 3 The dependencies of η_{sp}/c versus c in chloroform solutions of **a** DAB–dend–$(CN)_x$ and **b** DAB–dend–$(C15)_x$. The *numbers* indicate the number of generations

branched comblike molecules and star molecules [51–53]. The contributions of these effects can change depending on the number of end groups.

For the dendrimer series the translational scaling index was found to be close to the value corresponding to that of rigid spheres. This simplest model is used in the following interpretation. The hydrodynamic radii of the dendrimer molecules were calculated from the translational diffusion coefficient, D, according to the Stokes–Einstein equation [50, 54]:

$$R_D = kT/6\pi\eta_0 D\ .$$

The values of R_D for the two dendrimer series as well as the values of the volumes calculated from the R values are listed in Table 3. This table also gives the values obtained previously by the same procedure for lactodendrimers based on poly(propylene imine): DAB–dend–$(lacto)_x$ [29, 30]. The values of R_D for all the generations are in the order: $R_D^{CN} < R_D^{C15} < R_D^{LD}$.

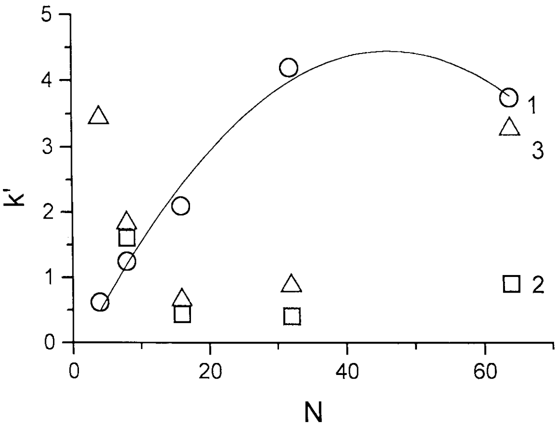

Fig. 4 The dependence of the Huggins parameter k' on the number of end groups in DAB dendrimers: *1* DAB–dend–$(CN)_x$, *2* DAB–dend–$(C15)_x$, *3* DAB–dend–$(lacto)_x$ [29, 30]

The hydrodynamic radii can also be calculated from viscometric data and molecular weights according to the equation [50, 54]

$$R_\eta = (3/10\pi N_A)^{1/3}(M[\eta])^{1/3}\ .$$

In this case, the R_η values will be correct if the molecular weight is determined by an absolute method. This also gives the possibility to estimate the real experimental error of these R_η values. It is known that the experimental values of the dendrimer molecular weight sometimes do not coincide with the theoretical ones [4, 11, 17]. In our case the quantitative evaluations were made on the basis of the diffusion coefficient measurements. Nevertheless the estimation of R_η values with the theoretical value of the molecular weights and experimental values of the intrinsic viscosity qualitatively correlate with those on the basis of the translational diffusion coefficients.

The molecular volumes of the dendrimer may be estimated using the hydrodynamic radii (Table 3). The hybrid dendrimer molecules have a greater volume than the initial dendrimers. This may be caused by either the contribution of the end groups themselves and/or by a possible increase in core volume; however, it should be taken into consideration that dendrimers based on poly(propylene imine) are short-chain dendrimers as well as dendrimers based on poly(amidoamine), for which the distance between two neighbouring branching points is small. The distance between two neighbouring branching points in the chains of poly(propylene imine) dendrimers is $l = 5 \times 10^{-8}$ cm. As a lower limit for estimates of the rigidity of a linear noncharged chain of a poly(propylene imine) analogue, we can take the rigidity of an aliphatic chain without bulky substituents. The Kuhn segment length for such a chain is $A = 20 \times 10^{-8}$ cm [48]. This implies that $l/A < 1$ and even the fifth generation has the chain length of a single

Table 3 Hydrodynamic radii and volumes of DAB–dend–(CN)$_x$, DAB–dend–(C15)$_x$ and DAB–dend–(lacto)$_x$ calculated from translational diffusion data of dendrimer molecules in solutions. N is the number of end groups

N	$(R_D \pm \Delta R_D)^{CN}$ (× 10^8 cm)	$(R_D \pm \Delta R_D)^{C15}$ (× 10^8 cm)	$(R_D \pm \Delta R_D)^{LD}$ (× 10^8 cm)	$(V_D \pm \Delta V_D)^{CN}$ (× 10^{21} cm^3)	$(V_D \pm \Delta V_D)^{C15}$ (× 10^{21} cm^3)	$(V_D \pm \Delta V_D)^{LD}$ (× 10^{21} cm^3)
4	4.8 ± 0.1	8.3 ± 0.4	13.8 ± 0.4	0.46 ± 0.02	2.4 ± 0.3	11.0 ± 0.9
8	8.2 ± 0.2	14.1 ± 0.3	16.7 ± 0.5	2.3 ± 0.15	11.7 ± 0.8	20 ± 1.5
16	11.9 ± 0.1	17.2 ± 0.6	19.9 ± 0.7	7.1 ± 0.25	21 ± 2	33 ± 3.5
32	17.6 ± 0.2	19.7 ± 1.8	28.7 ± 0.6	23.0 ± 0.9	32 ± 9	99 ± 6.5
64	20.7 ± 0.6	24.5 ± 1.0	36.2 ± 1.1	37 ± 3	62 ± 8	200 ± 18

dendron ($L = 25 \times 10^{-8}$ cm) comparable with the Kuhn segment length. It is necessary to take into account a possible increase in the equilibrium rigidity, A, caused by the interaction between side chains [8, 29, 53] in the dendron and by electrostatic interaction [55], which can lead to $l/A \ll 1$. This implies that the increase in the hybrid dendrimer size due to core swelling is unlikely and that to a first approximation all changes can be considered to be caused by the contribution of end groups. Considering DAB–dend–(CN)$_x$ to a first estimation as initial dendrimers for DAB–dend–(C15)$_x$ and DAB–dend–(lacto)$_x$ it is possible to calculate the additional volume occupied by the molecules of hybrid dendrimers. This volume is calculated as the volume of a spherical layer:

$$\Delta V_{C15} \equiv \left(V_G^{C15} - V_G^{CN}\right) = (4\pi/3)\left(R^3_{C15} - R^3_{CN}\right)$$

and

$$\Delta V_{LD} \equiv \left(V_G^{LD} - V_G^{CN}\right) = (4\pi/3)\left(R^3_{LD} - R^3_{CN}\right) \ .$$

The relations of the ΔV_{C15} and ΔV_{LD} values with the number of end groups for DAB–dend–(C15)$_x$ and DAB–dend–(lacto)$_x$ are shown in Fig. 5. To a first approximation these dependencies may be considered to be linear. This implies that nearly the same volume (independent of generation number) corresponds to one end group. Moreover, the volume, $\Delta V_{LD}/N = (2470 \pm 20) \times 10^{-24}$ cm^3, available for one lactose group in a lactodendrimer and to one end group in DAB–dend–(C15)$_x$ corresponds to the volume $\Delta V_{C15}/N = (400 \pm 20) \times 10^{-24}$ m^3. Although the contour length of the palmitoyl group is twice greater than that of the lactose group, the volume occupied by DAB–dend–(C15)$_x$ is smaller than that of the corresponding DAB–dend–(lacto)$_x$. Similarly, the volume per end group in DAB–dend–(C15)$_x$ is smaller than the volume per end group in DAB–dend–(lacto)$_x$.

Let us now compare the volumes accessible to the end groups in dendrimers with those occupied by one lactose molecule and one molecule corresponding to the palmitoyl group. The volume of a lactose molecule can be evaluated by using data on lactose translational diffusion in water. This measurement gives a translational diffusion coefficient (Fig. 6) of $D = (44.0 \pm 0.5) \times 10^{-7}$ cm^{2}s^{-1}, which in turn leads to a value of the Stokes hydrodynamic radius of $R = (5.7 \pm 0.06) \times 10^{-8}$ cm and, correspondingly, to the volume of an equivalent sphere of $V_{lacto} = (780 \pm 25) \times 10^{-24}$ cm^3. Hence, the volume per lactose group in DAB–dend–(lacto)$_x$ is 3.2 times greater than that occupied by an isolated lactose molecule in solution.

The palmitoyl group was simulated by a normal alkane $C_{18}H_{38}$. To evaluate the size of the n-alkane C18, the results of previous work [56, 57] are used. In these earlier studies, the translational diffusion coefficients were measured for a series of n-alkanes from $n = 5$ to $n = 32$ in benzene and in CCl$_4$. The data from these investigations can be considered as a single representation in the following system of axes: the characteristic diffusion coefficient, $[D] \equiv D\eta_0/T$, as a function of the number of carbon atoms, n, in the chain. This dependence may be described by the following empirical equation,

$$[D] \times 10^{10} = 1.264 + 3.588 \exp\left(\frac{n - 5.042}{8.970}\right) \ ,$$

from which one can calculate the corresponding values of the diffusion coefficient and the hydrodynamic radius for C18. This leads to the evaluation of the Stokes radius for C18: $R_{C18} = (3.5 \pm 0.04) \times 10^{-8}$ cm and, correspondingly, $V_{C18} = (180 \pm 6) \times 10^{-24}$ cm^3. Consequently, the volume per end group in DAB–dend–(C15)$_x$ is 2.2 times greater than that occupied by a free molecule corresponding to the end group.

Therefore, the larger volume occupied by DAB–dend–(lacto)$_x$ than that occupied by DAB–dend–(C15)$_x$ is caused by the considerable coiling of aliphatic groups compared to that of lactose groups. One cannot, however, rule out the fact that the possible incompatibility between the lactose groups and the core of the initial dendrimer can also influence the size of the lactodendrimers. In the case of DAB–dend–(C15)$_x$ the total end group length, L, corresponds to the n-alkane C22 contour length. So $L = 27.5 \times 10^{-8}$ cm, $L/A \approx 1.4$ and the initial back folding of the end groups becomes probable.

Hence, the comparison of the sizes of DAB–dend–(CN)$_x$ with those of DAB–dend–(C15)$_x$ and DAB–dend–(lacto)$_x$ molecules shows that the volume of the

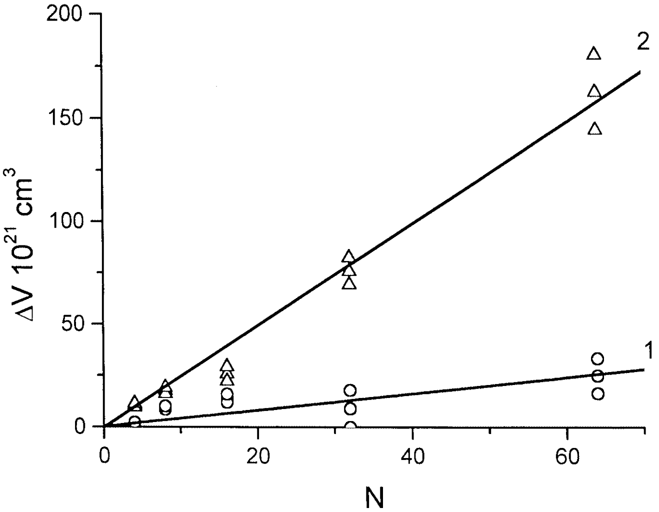

Fig. 5 Excess volume, ΔV, occupied by DAB–dend–$(C15)_x$ (*1*) and occupied by DAB–dend–$(\text{lacto})_x$ (*2*) in comparison with the volume occupied by DAB–dend–$(CN)_x$ molecules versus the number of end groups, *N*. Different points for the same *N* values indicate the error in the estimation of ΔV

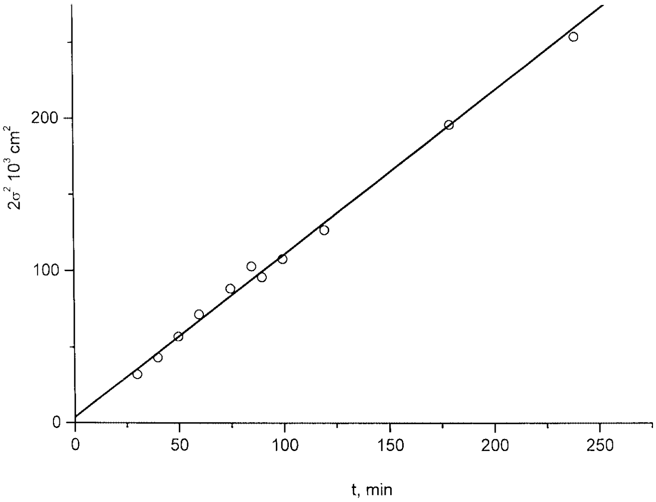

Fig. 6 The dispersion of diffusion boundary $2\sigma^2$ versus *t* for lactose molecules in water

external layer of end groups of the hybrid dendrimers exceeds the volume of free molecules corresponding to these end groups.

It is also useful to compare the volume per end group in the hybrid dendrimer molecules with the volume which a free molecule modelling the end group can exclude for its unbounded neighbours in solution. In fact, the excluded volume due to pair interactions of independent particles is proportional to their own volume, V_{proper} [54, 58, 59]: $V_{\text{excl}} = 8\nu V_{\text{proper}}$, where the proportional coefficient ν reflects the effects of shape asymmetry of the colliding particles. It ranges from $\nu = 1$ for a sphere to $\nu = 0.25(l/d)$ for a rod ($l \gg d$, where l is the rod length and d is the rod diameter). In the intermediate region for a cylinder of length l and diameter d, ν is calculated from [58] $\nu \equiv (1/4P)[\pi/4 + (\pi + 3)P/2 + P^2]$, where $P \equiv l/d$.

In our case, the asymmetry of groups attached to the dendrimer core does not exceed $P < 2$. Hence, the volume which one independent molecule corresponding to an end group excludes for other identical molecules in solution is $V_{\text{excl}} \approx 8V_{\text{proper}}$. In the case of DAB–dend–$(C15)_x$ V_{excl} is $1{,}440 \times 10^{-24}$ cm^3 and for DAB–dend–$(\text{lacto})_x$ this volume is $6{,}200 \times 10^{-24}$ cm^3. Consequently the available volume per lactose group in lactosylated poly(propylene imine) dendrimers is 3.2 times greater that the volume of the free lactose molecule but is 2.5 times less than the volume excluded by the free molecule corresponding to the end group. The available volume per end group in DAB–dend–$(C15)_x$ is 2.2 times greater that the volume of the free end molecule but is 3.6 times less than the corresponding excluded volume. This result indicates that the end groups in the hybrid dendrimer molecules exhibit some steric hindrance.

Since the volume of the hybrid dendrimers compared to that of the initial dendrimers increases proportionally to the number of end groups, in our opinion, the end groups are predominantly located on the periphery of each molecule, thus ensuring this volume will increase. The same conclusion was obtained from the results of small-angle neutron scattering experiments on poly(amido amine) dendrimers using deuterium labelling and scattering contrast variation [21, 60, 61], and also by Brownian dynamics simulation [62].

Now let us compare the value of $[\eta]$ with the volumes calculated on the basis of the translational friction coefficients. We suppose that the structure of the initial DAB dendrimers is perfect and that the substitution of the amine groups of the initial DAB dendrimers by CN, palmitoyl or lactose residues is complete; therefore, we use the calculated values of the molecular weights.

The general relationship for the intrinsic viscosity is

$$[\eta] = (RT/\eta_0 M D_r)(F/6) = F(N_A V/M) ,$$

where D_r is the rotational diffusion coefficient and F is a dimensionless coefficient depending on coil asymmetry, mass distribution and the permeability of moving molecular particles. In the case of a rigid sphere, this coefficient is 2.5. The data can be easily compared in the $M[\eta] - V$ coordinate system (Fig. 7).

Dashed line 3 corresponds to rigid spheres ($F = 2.5$) and line 4 corresponds to Gaussian coils in the θ condition ($F = 1.32$). For all the dendrimer series direct proportionality is observed, but the F values are different from 2.5. We have $F = 4.15$ for DAB–dend–(C15) and $F = 1.9$ for both DAB–dend–(CN) and DAB–dend–(lacto). This means that the sphere model does not make it possible to connect completely the translational and rotational friction data. This may be caused by molecule asymmetry, nonspherical mass distribution in

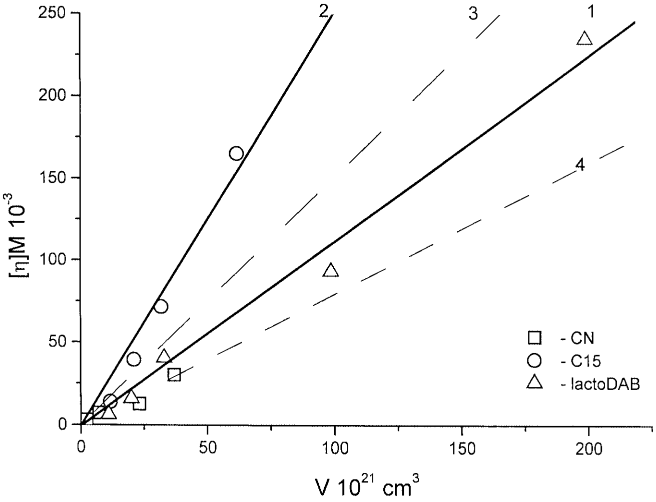

Fig. 7 The dependence of $[\eta]M$ versus V for DAB–dend–$(CN)_x$ (*1*), DAB–dend–$(C15)_x$ (*2*) and DAB–dend–$(lacto)_x$ (*1*). *3* corresponds to rigid spheres, *4* to Gaussian coil

the moving dendrimer molecules and their partial draining by solvent molecules, especially in the peripheral parts of the dendrimers. It is noteworthy that the discrepancy between the size estimation on the basis of the translational friction data and the intrinsic viscosity data (rotational friction) is usually also observed for a linear polymer chain.

Conclusions

The use of an experimental technique such as translation diffusion makes it possible to investigate dendrimers of all generations. The translation diffusion coefficient is a hydrodynamic characteristic sensitive to the dimension (and, hence, to the molecular weight) of dendrimers. The comparison of the diffusion coefficients of dendrimers with different end groups makes it possible to evaluate the contribution of these groups to dendrimer dimensions. The volume per end group exceeds that of free molecules which correspond to these end groups. The comparison of the experimental values of D and $[\eta]$ with the calculated molecular weight shows that for all dendrimer generations under investigation there is a corresponding linear correlation $M[\eta] \sim D^{-3}$; however, the rigid-sphere model is not completely adequate for the description of the hydrodynamic behaviour of dendrimer molecules.

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