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Rheology of Dendrimers. I. Newtonian Flow Behavior of Medium and Highly Concentrated Solutions of Polyamidoamine (PAMAM) Dendrimers in Ethylenediamine (EDA) Solvent

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ABSTRACT: Steady shear flow properties of an extensive family of dendrimers were examined for the first time in medium to high concentration solutions. For this, the first seven generations of ethylenediamine (EDA) core−polyamidoamine (PAMAM) dendrimers, having molecular weights from about 500 to almost 60 000 in 30 to 75 wt % solutions in ethylenediamine (EDA) were used. It was found that these dendrimer solutions exhibited typical Newtonian flow behavior as manifested by direct proportionality of the shear stress to the shear rate (i.e., constant viscosity with respect to both shear stress and shear rate) over the entire range of shear stress and shear rate studied. In addition to this, there was no abrupt change in the slope of the shear viscosity vs molecular weight relationship, indicating that these dendrimers do not interpenetrate to form transient quasi-networks of the “entanglement”-type typically found for long-chain linear or randomly branched macromolecules, nor do they engage in “sticking” interactions characteristic for the suspensions of idealized spherical particles. This rheological behavior is without precedence among high molecular weight synthetic polymers, and it is proposed that it is solely driven by the unique dendrimer macromolecular architecture which above a certain critical generation results in globular, nanoscopic spheroids whose outer surfaces close upon themselves and become impenetrable for other dendrimers or large molecules. The shear viscosity vs volume fraction dependencies showed that these dendrimers are draining to solvent molecules, but to a lesser extent than the corresponding random-coil type linear macromolecules of comparable molecular weights. These findings are consistent with a “dense-shell” model of dendrimer *intra*molecular morphology which can also explain their ability to encapsulate small molecular weight species in their “soft and spongy” interiors. From a typical Arrhenius-type temperature dependence of these dendrimer solutions viscosities and from the dependencies of their flow activation energy on molecular weight, it seems that the smallest kinetic unit involved in the dendrimer flow is the dendrimer molecule itself. Strong dependence of the dendrimer solution viscosity on concentration and temperature, as well as its independence on repeated loading, indicates substantial dendrimer flexibility and ability to deform. On the basis of these results and the supporting computer modeling calculations, it is proposed that the Newtonian flow behavior and the lack of an abrupt change of slope in the zero-shear viscosity vs molecular weight relationships represent characteristic “fingerprint” properties for dendrimers in general and that these properties distinguish these unique macromolecules from all other traditional classes of macromolecular architecture. It is also proposed that the critical degree of branching may be used as a defining structural criterion for distinguishing true dendrimers from their low molecular weight simple branched precursors.

Introduction

Dendritic polymers in general, and among them dendrimers in particular, have attracted outstanding scientific attention in recent years.[1] However, although the chemistry of these materials has matured to the level at which a large number of compositionally different families have been successfully synthesized and some are even commercially available, their full application potentials (particularly in materials science and engineering) will not be realized before the understanding of their physical properties is considerably more advanced. Toward this goal, some of the most intriguing but yet unresolved issues relate to dendrimer *intra*molecular morphology and *inter*dendrimer interactions. Undoubtedly, these properties will directly predetermine many macroscopic features and potential end uses of these new and unique polymers and are, therefore, not only of fundamental scientific importance but also of great practical value.

Dendrimers are a special type of highly branched macromolecules which are comprised of two or more treelike dendrons emanating from either a single central atom or atomic group, referred to as the core.[2] Ideally, a generalized structure of a tridendron dendrimer for example, can be represented as shown in Figure 1. The dendrons are built of branched repeat units, or branch cells, which are connected in a mathematically precise (i.e., geometrically progressive) architectural arrangement that gives rise to a series of regular, radially concentric layers of branch cells, called generations, organized around the core. As a consequence of such precise molecular organization, dendrimers can be prepared with an unusually high degree of synthetic control and structural monodispersity (including their molecular shapes and sizes[3]) even at truly “polymeric”, high molecular weights which can reach into several hundreds of thousands to a million.[1,2]

Experimental determination of exact shapes of dendrimers has turned out to be not an easy matter to resolve, primarily because most of the commonly used techniques reach their reliability limits in the size domain of lower dendrimer generations.[3] However, early computer modeling studies of ammonia−core polyamidoamine (PAMAM) tridendron dendrimers[4] pre-

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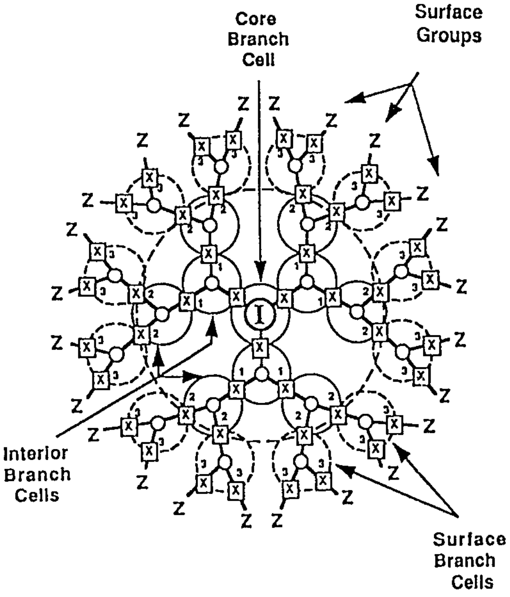


Figure 1. Schematic representation of a tridendron dendrimer including three basic building blocks of dendritic structure: the core branch cell, the interior branch cells, and the surface branch cells.

dicted that with increasing generation number these molecules develop through a continuum of shapes (referred to as "molecular morphogenesis"[5]) which range from fairly open "dome-shaped" or extended "platelike" structures at lower generations to "closed" spheroids at higher generations. This transition was observed between generations 2 and 5 by molecular dynamics calculations based on a force field acting on all atoms in equilibrated structures which showed a stepwise decrease in the ratio of the longest to shortest principal moments of inertia of these molecules (I_z/I_x) from about 4.5 at generation 1 to 1.3 at generation 4, where the value of 1 would correspond to a perfect sphere.[4] It was suggested that this shape change should result from steric congestion created by tethering of the dendron focal point while the terminal groups are amplified exponentially as a function of generation number.[4] A more recent study of the same type of dendrimers,[6] based on the moment of inertia values obtained by a Metropolis Monte Carlo molecular dynamics simulation,[7] showed a continuous decrease in the asphericity as a function of increasing generation number from 0.46 at generation 0 to 0.15 at generation 6, where the value of zero would correspond to an ideal sphere. Thus, it seems that dendrimers may never reach ideal sphericity even if grown from a pointlike core, such as a nitrogen atom in the case of ammonia−core PAMAMs but also that their deviations from this ideal shape should not be too large to prevent these unique molecules from being considered near-ideal spheroids.

Rheological flow behavior is one of the most important and characteristic macroscopic properties of fluids. In principle, it depends on (a) the molecular features, such as size, shape, density and flexibility and (b) the specific nature of the *inter*molecular interactions. Therefore, in addition to providing important engineering parameters for various applications and/or processing of materials, rheology may also represent a powerful analytical tool for determination of many fundamental molecular-level structural properties.[8] In fact, some of this information, particularly when relating to the nature of *inter*molecular interactions, may be difficult or even impossible to obtain in any other way.[8] However, in the field of dendrimer research rheology has not yet been applied to its full potential. Some information exists in the literature on dilute solution viscometry of various dendritic materials, but even this has been limited mostly to the relationships of intrinsic viscosity and hydrodynamic size on molecular weight or generation.[1,9,10] The only exceptions to this are some preliminary data that we published from this study[11,12] and a paper on the bulk rheology of polybenzyl ether dendrimers by Hawker and co-workers.[13]

Here, we report on the results obtained from a rheological study of the first seven generations (i.e., generations 0 through 6) of Starburst ethylenediamine (EDA) core−polyamidoamine (PAMAM) dendrimers,[2] in the medium (i.e., from about 30 wt %) to high (i.e., to about 75 wt %) concentrated solutions in ethylenediamine (EDA) solvent. This concentration range was chosen in order to maximize the intensity of *inter*dendrimer interactions that may be present in these systems and EDA was selected because it represents a good solvent for these dendrimers. In addition, we also describe the first direct comparison of one physical property of an extensive dendrimer family (i.e., the viscosity−molecular weight relationship) with the same property of the corresponding compositionally identical linear polymer of comparable molecular weights.

Ethylenediamine (EDA)−core PAMAM dendrimers differ from their ammonia-core counterparts in that a single nitrogen core atom of the ammonia−core is replaced by a somewhat more elongated $>N-(CH_2)_2-N<$ unit and a fourth dendron is added to the overall structure, as illustrated in Figure 2. However, although these structural differences may be expected to distort the overall molecular shapes of EDA−core PAMAM dendrimers into slightly more ellipsoidal forms than those of their ammonia−core counterparts, they do not seem large enough to affect significantly many of their macroscopic properties, such as rheological flow behavior of interest to this study.

Various results from small angle neutron[14] and X-ray scattering[3] studies, size exclusion chromatography, and dilute solution viscometry measurements[1a,2,9,10] have shown that dendrimers occupy the lower part of the nanoscopic size domain, ranging in molecular diameters from about 1 to about 15 nm, as shown in Table 1.[2] In fact, as the result of highly controlled growth during the synthesis (see Figure 2), dendrimer sizes increase with increasing generation in regular intervals of about 1 nm per generation. Thus, it follows from the available data that particularly at higher generations, dendrimers provide a unique combination of (a) high molecular weights typical for classical macromolecular substances, (b) molecular shapes similar to idealized spherical particles, and (c) nanoscopic sizes that are larger than those of the small molecular weight compounds but smaller than those of typical macromolecules.[15] As such, dendrimer solutions indeed represent unique fluids which combine structural properties of true macromolecules with spherical shapes of suspension particles within the nanoscopic size domain that have not been available for rheological study before.

Experimental Section

Dendrimers and Their Solutions. The first seven generations (i.e., generations 0 through 6) of ethylenediamine

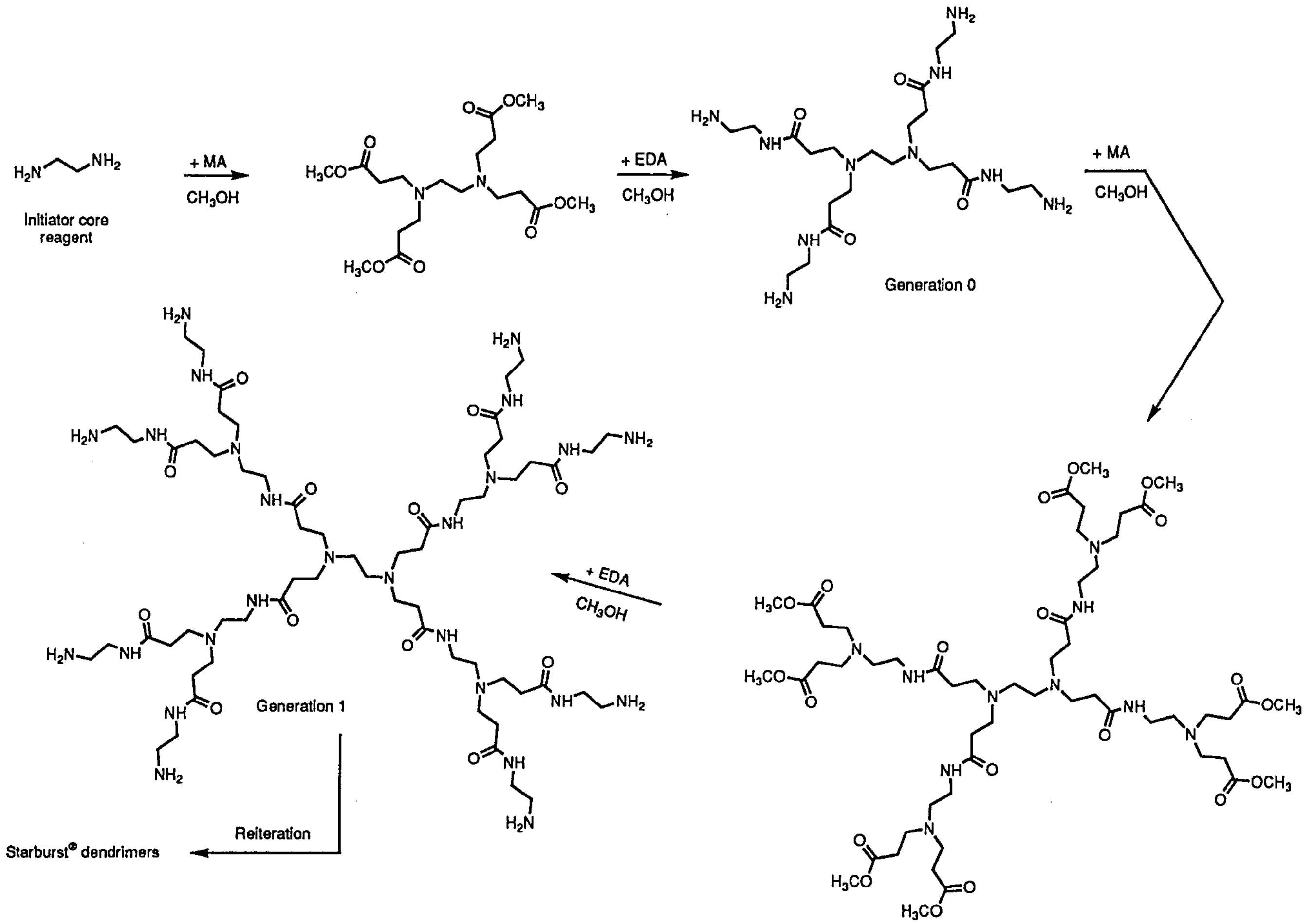


Figure 2. Preparation of Starburst, ethylenediamine (EDA) core–poly(amidoamine) (PAMAM) dendrimers. Starburst is a registered trademark of Dendritech Inc.

Table 1. Selected Characteristics of EDA Core PAMAM Dendrimers

generation	no. of surface groups[a]	mol wt[a]	dendrimer radius, Å[b]: hydrodynamic radius, R_h (by DSV)[c]	dendrimer radius, Å[b]: radius of gyration, R_g (by SANS)[d]	R_g/R_h[e] SANS/DSV	bulk density,[f] g/cm^3
0	4	517				1.178
1	8	1430	10.1			1.196
2	16	3256	14.4			1.214
3	32	6909	17.5	16.5	0.943	1.219
4	64	14215	25.0	19.7	0.788	1.224
5	128	28826	32.9	24.3	0.739	1.220
6	256	58048		30.3		
7	512	116493		35.8		

[a] Nominal values calculated for ideal dendrimer growth. [b] At 25 °C; in 0.1 molar citric acid in water; at pH = 2.7. [c] DSV = dilute solution viscometry. Values were calculated from experimental intrinsic viscosity data of ref 9. [d] SANS = Small angle neutron scattering. Data from ref 14. [e] For nondraining "hard spheres", $R_g/R_h = 0.775$; for free-draining random coils, $R_g/R_h = 1.143$. [f] At 20 °C. Maximum error: ±0.68%.

(EDA) core–polyamidoamine (PAMAM) dendrimers, obtained from Dendritech, Inc. (Midland, MI) were used in this work. These dendrimers were prepared by the well-known "excess-reagent" divergent growth method involving a reiterative reaction sequence consisting of (a) Michael addition reaction of methyl acrylate (MA) to amines and (b) amidation reaction of the resulting methyl ester precursors with ethylenediamine (EDA), as illustrated in Figure 2 and described in detail elsewhere.[8,16] The samples used in this work were obtained as methanol solutions and were thoroughly dried before testing until no detectable amounts of solvent could be found by thermogravimetric analysis (TGA). In the dry state, the first three generations (i.e., generations 0 through 2) were viscous liquids, while higher generations (i.e., generations 3 through 6) were amorphous solids. Selected molecular characteristics of these PAMAM dendrimers are summarized in Table 1.

The dendrimer/EDA solutions were prepared from dry dendrimers and twice distilled EDA (T_{bp} 118 °C, obtained from Aldrich). For all generations, the highest concentration solution (i.e., 75 wt %) was prepared first and the less concentrated ones were then obtained by diluting the stock. The lowest concentration solutions were about 30 wt %, and the maximum error involved in the weight measurements was less than 0.01 g (i.e., less than 0.1% in weight concentration).

Steady Shear Rheometry. Steady shear rheometry of all dendrimer solutions was performed using a Carri-Med CSL-100 stress-controlled cone-and-plate rheometer, with version 5.0 software for data acquisition. The cone diameter was 4 cm, and the cone angle was 2°. The precision of the viscosity readings ranged from ±1 P for the highest to $\pm 1 \times 10^{-4}$ P for the lowest viscosities recorded. Measurements were performed over a shear stress range from 10 to 10^3 dyn/cm^2 (correspond-

Table 2. Zero-Shear Viscosities of EDA Core PAMAM Dendrimer EDA Solutions as a Function of Concentration and Temperature

concentration, wt %	viscosity, P						
	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C
			Generation 0				
29	0.10	0.09	0.07	0.07	0.06	0.06	0.06
37	0.21	0.18	0.15	0.13	0.11	0.10	0.09
50	0.70	0.55	0.45	0.38	0.32	0.29	0.25
60	2.15	1.64	1.29	1.03	0.87	0.78	0.74
75	18.97	12.23	8.28	5.86	4.47	3.31	2.68
			Generation 1				
30	0.18	0.16	0.14	0.12	0.11	0.10	0.09
40	0.64	0.51	0.42	0.36	0.31	0.27	0.25
50	2.68	2.05	1.65	1.33	1.12	0.96	0.85
60	12.79	8.67	6.18	4.56	3.50	2.79	2.33
75	340.9	191.5	113.6	69.82	44.93	30.06	21.18
			Generation 2				
30	0.32	0.28	0.24	0.21	0.19	0.17	0.16
40	1.15	0.95	0.81	0.70	0.63	0.57	0.56
51	5.42	4.10	3.23	2.57	2.09	1.91	1.88
57	26.72	18.38	13.02	9.38	7.16	5.82	5.06
75		560.3	329.3	198.1	124.1	81.72	54.79
			Generation 3				
40	--	1.46	1.19	0.97	0.84	0.75	0.69
50	--	6.62	5.08	4.21	3.50	3.15	2.87
60	--	36.23	25.42	18.43	14.02	11.01	9.50
75	--	1083	621.6	371.1	229.2	147.4	99.99
			Generation 4				
30	0.64	0.53	0.46	0.40	0.35	0.32	0.29
40	3.42	2.68	2.16	1.79	1.51	1.30	1.17
50	12.54	9.75	7.75	6.15	5.03	4.25	- -
58	64.76	45.74	33.45	24.85	19.26	15.82	14.59
75	4617	2524	1462	864.9	541.0	355.9	242.2
			Generation 5				
30	1.01	0.81	0.68	0.58	0.50	0.46	0.43
40	5.49	4.23	3.37	2.87	- -	- -	- -
50	22.61	17.06	14.13	12.14	10.11	8.70	7.67
60	129.4	86.63	60.46	44.21	36.63	28.02	22.16
75	5274	2871	1641	971.1	600.3	384.0	257.2
			Generation 6				
30	1.58	1.34	1.13	0.97	0.85	0.75	0.69
40	7.67	5.95	4.73	3.90	3.31	2.94	2.82
50	45.30	33.04	24.49	18.26	14.00	11.13	9.44
59	205.1	137.2	95.39	68.38	49.96	37.75	29.53
75	7523	4185	2405	1450	921.3	601.1	409.5

ing to almost six decades of the shear rate range from 1 × 10^{-2} to 1.5 × 10^{3} s^{-1}). Shear stress was applied in logarithmic increments over 20 min of measurement time. Since amine terminated PAMAM dendrimers are highly hygroscopic, all measurements were performed in a nitrogen atmosphere, using an attached trap to prevent evaporation of the solvent.[9] Temperature control was accurate to ±0.2 °C, and the PAMAM dendrimer stability under these experimental conditions was verified by repeated rheological testing, ^{13}C NMR and size exclusion chromatography (SEC) before and after shear stressing, and thermogravimetric analysis (TGA).

Computer Modeling. Computer-generated molecular models were constructed using the Builder module in version 4.0.0 of the Molecular Simulations, Inc. (MSI) Insight molecular modeling software. Dendrimers were built by successively adding methyl acrylate and ethylenediamine fragments to "growing" structures of appropriate size (i.e., dendrimer generations) in a manner analogous to the divergent growth strategy used in the actual synthesis. Energy minimization was allowed to run to the default cutoff value of the MSI software (derivative = 0.01) after the addition of each small molecular fragment. Subsequent molecular dynamics runs were carried out on the energy minimized structures at 300 K for 50 ps. In all cases the potential energy profiles reached a plateau level well before the calculation cutoff time. All energy minimization and molecular dynamics calculations were carried out using the consistent valence force field (CVFF) available in MSI's Discover software and a Silicon Graphics, Inc. (SGI) Indigo workstation which was run under version 5.3 of SGI's IRIX operating system.

Results and Discussion

Steady Shear Flow of EDA−Core PAMAM Dendrimer Solutions in EDA. Steady shear flow of 34 different solutions of the first seven generations of EDA-core PAMAM dendrimers (i.e., from generation 0 through generation 6) in ethylenediamine (EDA) solvent was investigated using a cone-and-plate rotational rheometer at seven different temperatures which ranged from 10 to 40 °C in 5 °C intervals.[9] At each temperature and for each dendrimer generation (except for generation 3, as shown in Table 2), five different solution concentrations ranging from about 30 to 75 wt % in increments of about 10 wt % were examined. As examples of the results obtained, shear stress vs shear rate plots for the two limiting cases of this study: generation 0 (molecular weight of about 500) at the lowest solution concentration (i.e., 29 wt %) and generation 6 (molecular weight of almost 60 000) at the highest solution concentration (i.e., 75 wt %), are shown in Figure 3. The corresponding

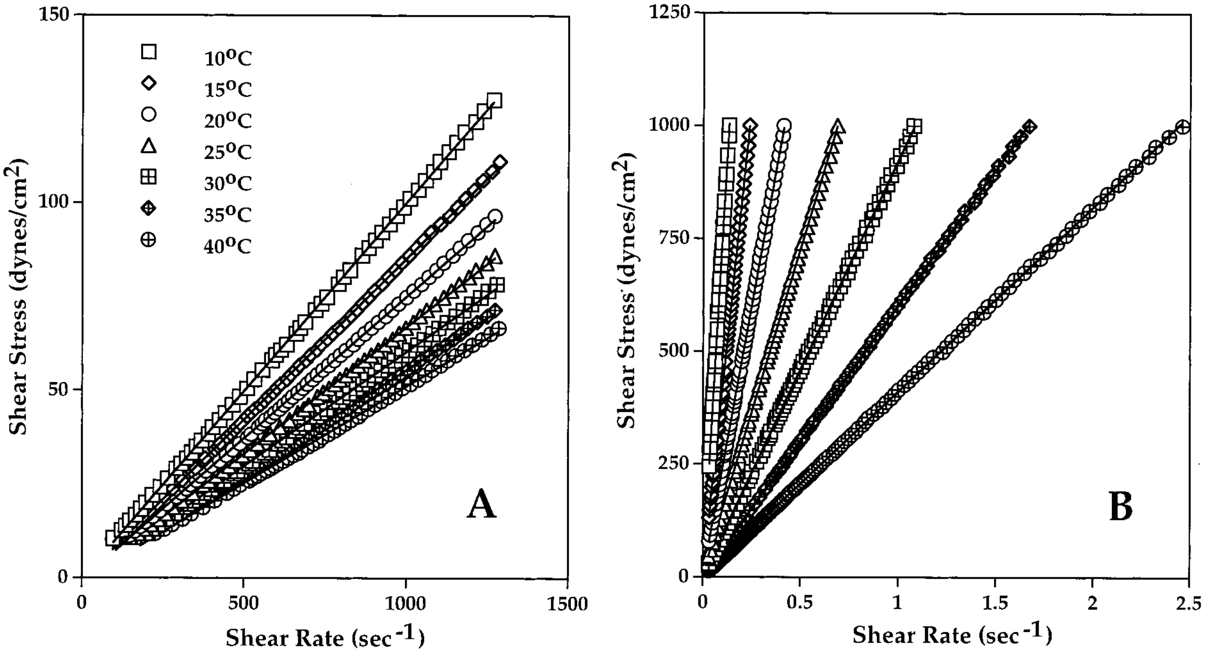


Figure 3. Shear stress vs shear rate relationships of generation 0 and 6 ethylenediamine (EDA) core–poly(amidoamine) (PAMAM) dendrimers in ethylenediamine (EDA) solvent at indicated temperatures. Key: (A) generation 0, 29 wt % solution; (B) generation 6, 75 wt % solution.

responses of all other dendrimer solutions varied between these two extremes with respect to both dendrimer generation and solution concentration, but all exhibited the same linearity of this rheological function.

As illustrated in Figure 3, over the entire range of evaluated shear stresses or shear rates, all of the examined PAMAM dendrimer/EDA solutions showed linearity between the shear stress (σ) and shear rate ($\dot{\gamma}$) and showed constant viscosity (η) with respect to both shear stress and shear rate. To illustrate the latter, a plot of viscosity vs shear rate for 40 wt % solutions of all seven PAMAM generations at 25 °C is shown in Figure 4, while a complete list of viscosity values determined for all examined dendrimer solutions at all concentrations and temperatures is given in Table 2.

It can be seen from these figures that the flow behavior of all of these dendrimer solutions was typical of Newtonian fluids and fundamentally different from either that of the vast majority of high molecular weight chain polymers (both in solutions and in bulk[17]) or that of the suspensions of spherical particles,[18,19] which both generally show "shear-thinning" above some critical shear rate (or shear stress), molecular weight, and/or concentration.[20] This clearly indicates that the reasons responsible for non-Newtonian flow behavior of chain polymers and suspensions of spherical particles must be absent from dendrimer solutions even at molecular weights as high as 60 000 and solution concentrations as high as 75 wt %. For the chain-type polymers of comparable molecular weights (including linear, randomly or regularly branched, cyclic, star-shaped, and H-shaped ones[20]), these reasons are generally associated with the establishment of "entanglement"-type interactions and the resulting formation of transient quasi-networks.[17] On the other hand, for the suspensions of spherical particles, they originate from the tendency of individual particles to aggregate into doublets or multiparticle agglomerates depending on concentration.[21] Hence, it follows from these results that, even at high molecular weights (i.e., generations) or solution concentrations, dendrimers do not undergo either of these two types of interactions nor do they cause any significant disturbance of the solvent flow, which would result in deviations from Newtonian flow behavior.[21] This finding is in complete agreement with the recently described small-angle X-ray scattering (SAXS) study, which showed no indication of *inter*dendrimer correlation at concentration of 26 wt % in methanol, another good solvent for these EDA–core PAMAM dendrimers.[3]

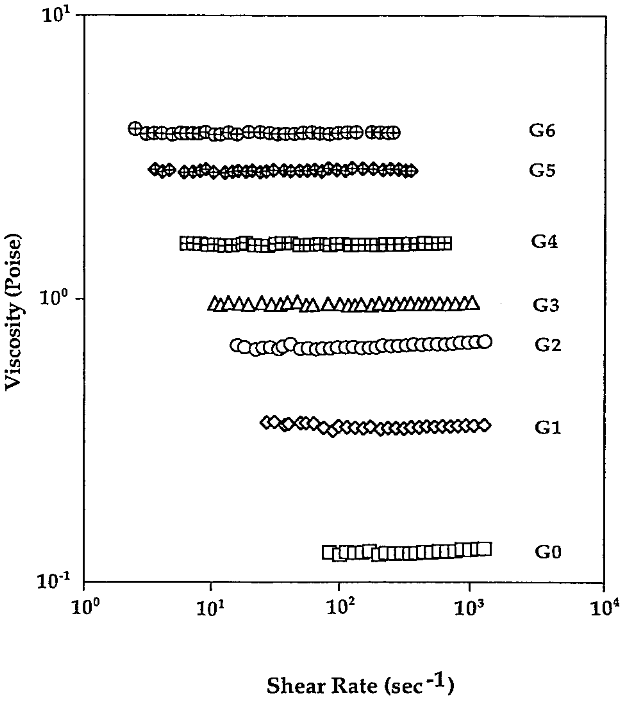


Figure 4. Viscosity vs shear rate relationships for the 40 wt % solutions of the first seven generations (i.e., generations 0 through 6) of ethylenediamine (EDA) core–polyamidoamine (PAMAM) dendrimers in ethylenediamine (EDA) solvent at 25 °C.

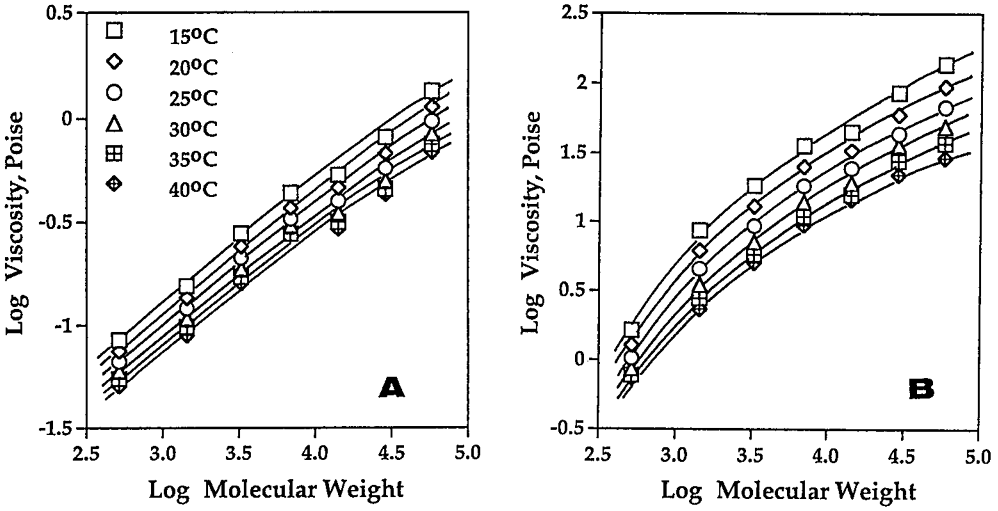


Figure 5. Viscosity vs molecular weight relationships for (A) 30 wt % and (B) 60 wt % solutions of the first seven generations of ethylenediamine (EDA) core-polyamidoamine (PAMAM) dendrimers in ethylenediamine (EDA) solvent at indicated temperatures.

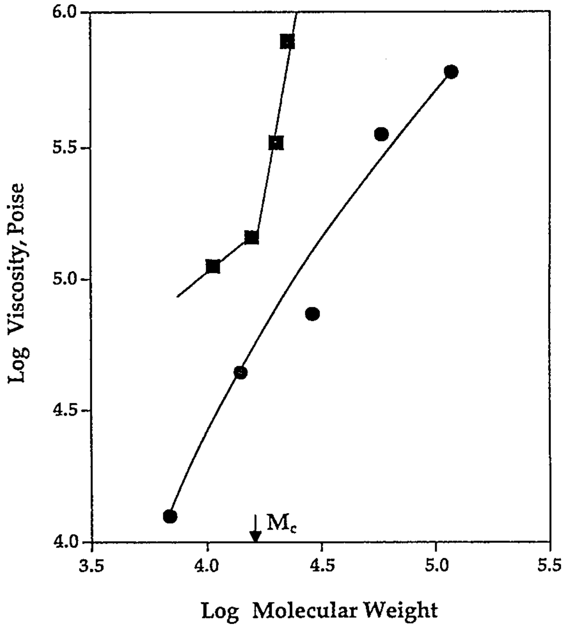


Figure 6. Comparison of zero shear viscosity vs molecular weight relationships for neat ethylenediamine (EDA) core–polyamidoamine (PAMAM) dendrimers (●) and linear polyamidoamine (■). Data were taken from oscillatory shear measurements at 95 °C. Molecular weights for linear PAMAM were obtained by size exclusion chromatography in water/citric acid buffer relative to linear poly(ethylene oxide) standards. All linear PAMAM samples had most probable molecular weight distributions, $\bar{M}_w/\bar{M}_n$, ranging between 1.8 and 2, and weight average molecular weights were used for this plot. M_c = 14 500 is the critical molecular weight for the onset of entanglement couplings in linear PAMAM.

It should be also noted that in another clear agreement with this, all examined dendrimer solutions showed viscosities which were considerably lower (i.e., by at least an order of magnitude or more) than the viscosities that are usually found for similar solutions of chain-type macromolecules of comparable molecular weights and concentrations.[11,12,17,22,23] Because the same difference was also observed when the behavior of bulk PAMAM dendrimers was compared to that of the linear polymer of the same chemical composition and comparable molecular weights (see Figure 6), it follows that spheroidal[3] nanoscopic dendrimers flow much more easily than their chain-type counterparts, suggesting intriguing potentials for their use in polymer processing and various other flow-related applications.

Shear Viscosity vs Molecular Weight Relationships of EDA–Core PAMAM Dendrimers in EDA Solutions and in Bulk. Figures 5 and 6 show shear viscosity vs molecular weight relationships for EDA–core PAMAM dendrimers in EDA solutions and in bulk, respectively. In addition, Figure 6 also includes the corresponding relationship between the zero-shear viscosity and weight average molecular weight of linear PAMAM in bulk. The results of Figure 6 were obtained by dynamic oscillatory shearing at 95 °C and under experimental conditions where neither PAMAM dendrimers nor the corresponding linear polymer showed any indication of thermal, thermo-oxidative, or mechanical instability.[9] To the best of our knowledge, this is the first direct comparison of one physical property of a linear polymer and its corresponding dendrimer counterparts where both have the same chemical composition and comparable molecular weights. The synthesis and other properties of this linear PAMAM will be described elsewhere.[24]

Several interesting features of the dendrimer viscosity–molecular weight relationships can be observed from these figures. First, while as expected linear PAMAM showed typical behavior of a high molecular weight polymer,[25] including the characteristic break in the slopes of the linear portions of the log η_o vs log $\bar{M}_w$ dependence at $\bar{M}_w$ of about 15 000, no such break appeared for dendrimers either in solutions (Figure 5) or in bulk (Figure 6). Therefore, since this break has been found for a variety of different macromolecular topologies, including linear, randomly or regularly branched, cyclic, multiarm star-shaped, or H-shaped polymers[20] and is traditionally associated with the critical chain length for entanglement formation,[25] these results further support the conclusion that dendrimers do not engage in such interactions.

Second, it can be also seen from Figure 6 that the slope of the linear polymer log η_o vs log $\bar{M}_w$ relationship changed from about 0.7 at lower molecular weights to about 4.5 above the critical molecular weight for entanglement formation (M_c), in agreement with expected semiflexible character of the PAMAM chain segments.[23] However, in a clear contrast to this, the corresponding log η vs log M relationship for bulk dendrimers was a smooth *curve* with local slopes gradually decreasing with molecular weight from about 1.9 between generations 3 and 4 (i.e., molecular weights between about 7 000 and 14 000, respectively) to about 0.7 between generations 6 and 7 (i.e., molecular weights between 58 000 and almost 120 000, respectively). In solutions (Figure 5), the shape of this dendrimer function remained the same, but the extent of curvature was clearly dependent on concentration and temperature, increasing with increase in both of these parameters. A similar log η vs log M relationship was also obtained by Hawker and co-workers for polybenzyl ether dendrimers in bulk,[13] with the main difference being that in that case the change in local slopes was even more dramatic and ranged from over 5 at lower molecular weights (i.e., between 1000 and 3000) to about 1.1 above a molecular weight of about 11 000.

Furthermore, this shape of dendrimer viscosity vs molecular weight relationship was distinctly different not only from the typical shape of the corresponding relationships for various chain-type polymers regardless of their molecular topology[20] but also from the steep linear relationship (i.e., slope > 10) obtained for the suspensions of spherical microgels which had comparable but nevertheless somewhat larger particle sizes than those of the dendrimers examined in this work (i.e., the hydrodynamic radii of these spherical microgels ranged from about 7 to about 28 nm).[20] Consequently, it appears that the viscosity−molecular weight relationship may represent a unique, characteristic "fingerprint" property of dendrimers, which is independent of their particular state (i.e., solutions or bulk) and/or chemical composition (i.e., polybenzyl ethers or PAMAMs). Instead, it seems to reflect their small (i.e., nanoscopic) sizes, compact molecular shapes, and lack of *inter*dendrimer interactions. Three main features of this relationship seem to include (a) a smooth, monotonically increasing curved shape with decreasing local slopes as a function of molecular weight (i.e., generation), (b) a limiting value of this slope approaching unity at high dendrimer generations, and (c) significantly lower viscosity values than those of the corresponding chain-type polymers of comparable molecular weights.

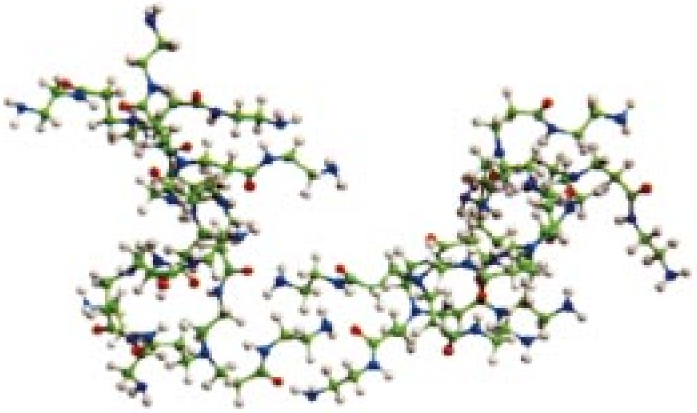
Third, it is indeed intriguing to note from Figure 6 that the part of the PAMAM dendrimer log η vs log M relationship between generations 6 and 7 in bulk appears as an almost exact extension of the corresponding linear polymer dependence at molecular weights below the critical molecular weight for entanglement formation. Not only do the two portions of these dependencies have identical slopes, but also even the respective viscosity values were very close to a single linear relationship with respect to molecular weight. However, whether this is just a coincidence or another consequence of unique dendrimer molecular architecture is impossible to judge on the basis of these data only.

Computer Modeling of Dendrimer Shapes. Parts a and b of Figure 7 show "frozen-in-time" computer-generated models of energy minimized pairs of PAMAM molecules of generations 1 and 4, respectively, which have been subjected to up to 50 ps of molecular dynamics at 300 K. In running these molecular dynamics calculations, the potential energy profiles leveled off after approximately 30−40 ps. The pairs of structures displayed in parts a and b of Figure 7 are representative examples obtained (i) between 40 and 50 ps through the dynamics runs and (ii) at the ends of the molecular dynamics calculations (at 50 ps). It should be noted, however, that the structures used herein for illustration represent only a few of the vast number of possible configurations. Averaged over time (particularly over much longer time periods which would correspond to the time scale of rheological measurements such as those performed in this work), the overall configuration of the dendrimer structures of Figure 7b would not be expected to contain any open "clefts" or "channels" as may appear from this figure. The size bar indicated in Figure 7 was obtained from a set of "molecular rulers" constructed from all-*trans* polymethylene chains of known or measurable dimensions.

The generation 4 PAMAM dendrimer models of Figure 7b strongly suggest that the outer surface of these dendrimers is "closed" upon itself or at least "dense" enough to act as an impenetrable barrier to other neighboring dendrimers or their parts. In contrast, Figure 7a illustrates that at lower generations this situation is essentially reversed and that *inter*molecular interpenetration of these molecules must be expected. In fact, representative structures of generation 1 PAMAM molecules clearly appear to be open "platelike" or "domelike"[11] entities which may readily permit a branch from a given molecule to penetrate into the interior of its nearest neighbor. In the case of PAMAMs of Figure 7a, this tendency is further enhanced by the expected establishment of *inter*molecular hydrogen bonds between the interior amide groups of two interpenetrating molecules or between the primary amine units of one molecule and the amide carbonyl oxygens of another. Clearly, this may represent an additional driving force for interpenetration of the low generation PAMAMs, resulting in their relatively high viscosities with respect to the molecular weights. Conversely, in the case of polybenzyl ethers,[13] it would be expected that π-stacking interactions between the aromatic rings may create a similar situation.

In contrast to this, however, upon closure of the dendrimer outer surface at higher generations, attractive *inter*molecular forces resulting from physical interpenetration should diminish and perhaps disappear at high enough generations. This would result in entanglement and/or aggregation free dendrimer solutions and/or bulks, which, in turn, would be expressed as experimentally observed Newtonian flow and viscosity vs molecular weight relationships. It would then be because of this reason that the flow of dendrimer systems (i.e., solutions as well as bulk dendrimers) is fundamentally different from that of the corresponding chain-type macromolecules (of comparable molecular weight and/or chemical composition) and suspensions of idealized spheres (of comparable sizes), as shown in the preceding sections. In fact, this would be essentially an architecturally determined dendrimer property and therefore specific for dendrimer's unique type of macromolecular organization.

Critical Degree of Branching. The hypothesis that described generationally dependent flow behavior of dendrimers may be their characteristic architecturally driven property[26] independent of particular chemical composition and state, arises from observation that both PAMAM and polybenzyl ether dendrimers showed analogous features of the respective rheological relationships. Furthermore, because the slopes of the log



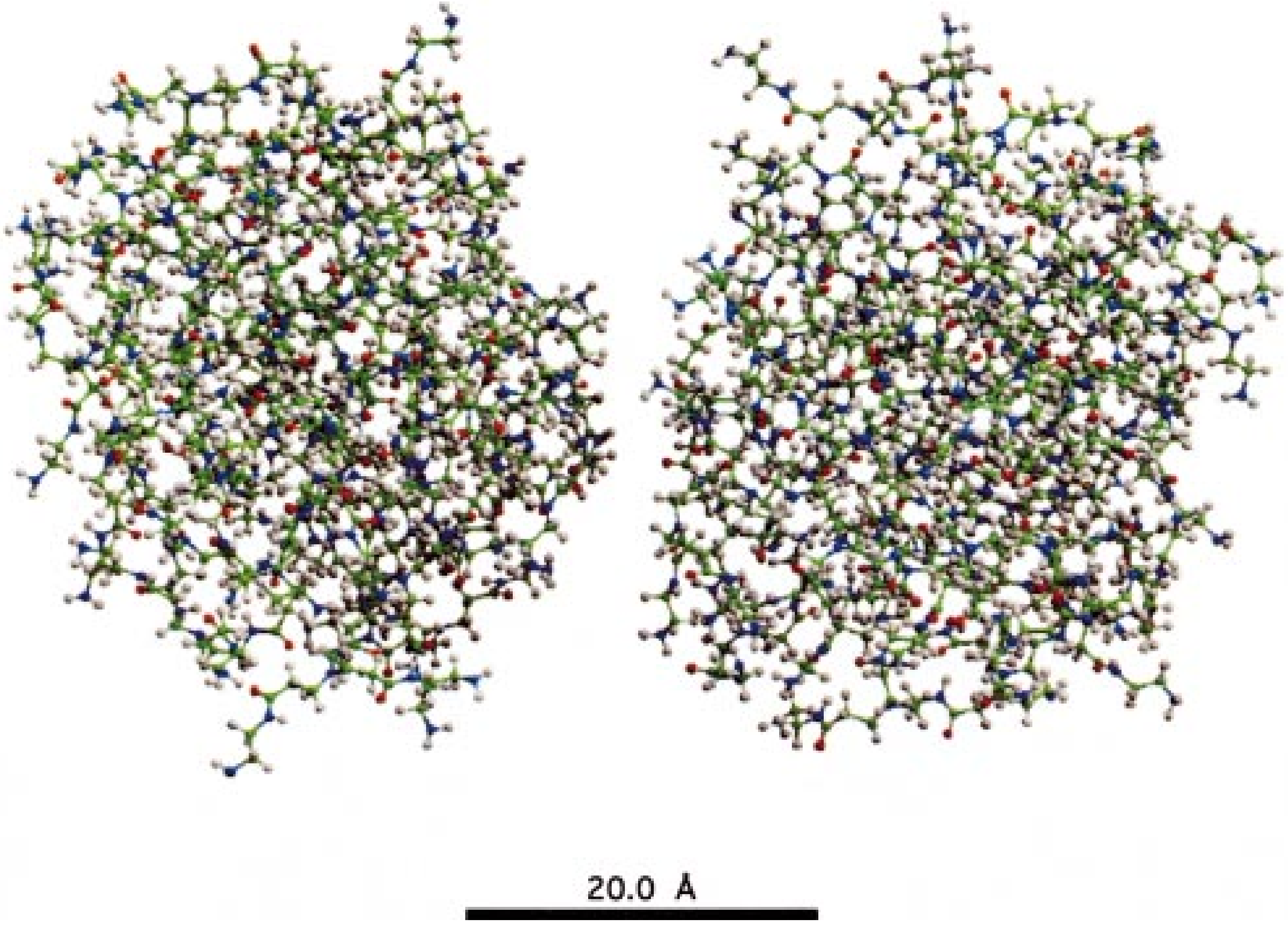


Figure 7. Computer-generated models of ethylenediamine (EDA) core−poly(amidoamine) (PAMAM) dendrimer precursors of generation 1 (a) and fully developed dendrimers of generation 4 (b) after 50 ps of molecular dynamics.

η vs log M relationships for both of these dendrimer families and for both PAMAM solutions and the bulk state showed similar decreases with generations and a tendency toward a common value of unity at high molecular weights (i.e., generations), it appears that the molecular level features that are responsible for this dendrimer behavior must be related to some critical generation size. From the computer modeling experiments described in the preceding section, this growth stage seems to be the generation at which the outer dendrimer surface begins to "close" upon itself and inhibit *inter*dendrimer interactions (i.e., interpenetra-

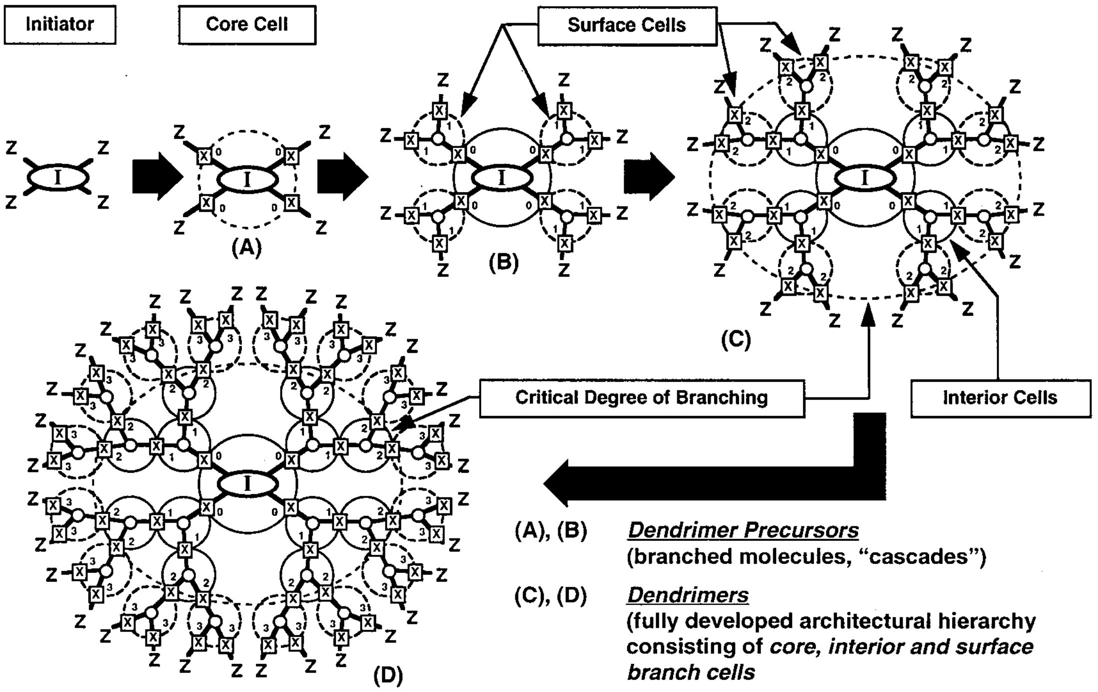


Figure 8. Critical degree of branching (CDB): a possible defining structural criterion for a dendritic macromolecule. Z represents the end groups.

tion involving neighboring dendrimers or their parts). In an attempt to pinpoint that particular "critical" generation at which this major structural transformation may onset during the course of dendrimer formation, Figure 8 shows a generalized schematic representation of the divergent dendrimer growth process. Of course, a similar analysis should also hold for the convergently prepared dendrimers.

It can be visualized from Figure 8 that the development of dendrimer structure during the course of the synthesis involves a transition from simple branched molecules (structures A and B of Figure 8) into fully developed true dendrimers (structures C and D of the same figure). A fully developed dendrimer is a molecule consisting of at least two dendrons emanating from a single, common core and containing all three fundamental building blocks which include the core branch cell, the surface branch cells, and the interior branch cells (see structure C of Figure 8). The transition from simple branched molecules to fully developed dendrimers occurs, therefore, at a synthesis stage which may be designated as the critical degree of branching (CDB) at which the resulting molecules contain for the first time in their synthetic history all three basic building blocks of the fully developed dendritic structure.[2] As can be seen from Figure 8, in the PAMAM dendrimer family the onset of this structural transition in molecular complexity (from B to C in Figure 8) coincides with the generation at which the stepwise decrease in the I_z/I_x aspect ratio was observed[4] (i.e., generation 2) and where the resulting molecules start changing their shape from open "dome"-like or "plate"-like to globular spheroids resulting in the closing of dendrimer outer surface upon its interior.[2]

From this, it follows that the lower generation dendrimer precursors should be quite open for *inter*molecular interpenetration (compare with Figure 7a) which, in the PAMAM case, should result in considerable *inter*molecular hydrogen bonding. In contrast to this, with an increase in generation the probability of such interactions would decrease and perhaps even disappear when the dendrimer outer surface effectively closes upon itself (i.e., apparently at about generation 4 as judged from Figure 7b and previous computer modeling results). Essentially, this would represent a reversed situation from what is normally found in typical chain polymers, where the probability of entanglements increases with an increase in the polymer chain length. Therefore, while the lower molecular weight members of a dendrimer homologous series would be expected to interpenetrate and interact more, resulting in the steeper slopes along the low molecular weight part of the log η vs log M relationships, the degree of interpenetration should decrease with increase in generation, leading to a corresponding decrease in the log η vs log M slope upon the "closure" of the dendrimer outer surface. Clearly, this is consistent with the trend that has been experimentally observed for both PAMAM (see Figures 5 and 6) and polybenzyl ether dendrimers (compare with ref 13). It is also consistent with the results of a recent SAXS study which indicate that generations 5 through 10 PAMAM dendrimers behave as particles with "rather sharp boundaries".[3]

In other dendrimer families, a similar structural analysis should reveal the generational stages at which the CDB criterion is satisfied. Thus, while the transition to a complete dendrimer hierarchy of branch cells may provide a general architectural criterion for distinguishing dendrimer precursors from true dendrimers, the generational CDB value at which this criterion is satisfied in a particular family of these molecules will be determined by the chemical composition and will be specific for that family. Acceptance of this structural criterion (i.e., the CDB) in considerations of highly branched dendritic compounds may help avoid continued confusion concerning the definition of dendrimer structure.

Dependence of Dendrimer Solution Viscosity on Concentration. Figure 9 shows a comparison of the shear viscosity–concentration relationships obtained for

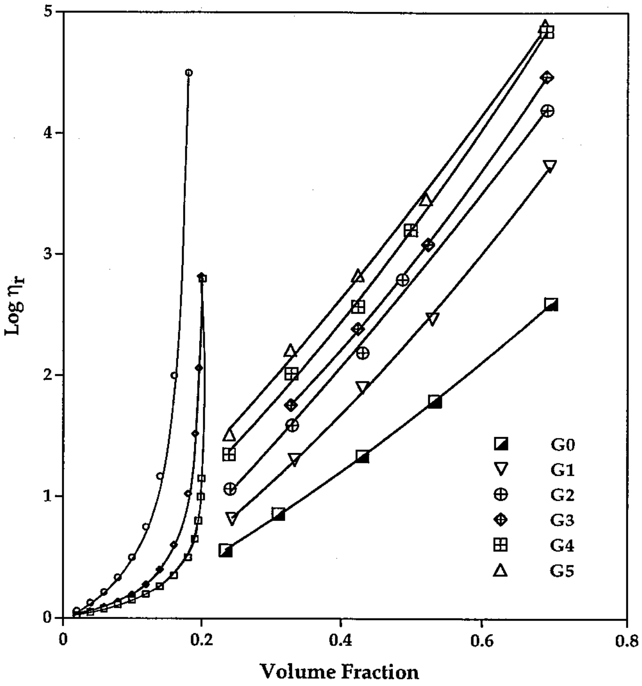


Figure 9. Comparison of the viscosity vs concentration dependencies of ethylenediamine (EDA) core−polyamidoamine (PAMAM) dendrimers in ethylenediamine (EDA) solutions with the model behavior of idealized "hard-sphere" suspensions at 20 °C and $\phi_p = 0.2$ maximum packing fraction. "Hard sphere" models include the following: (○) Mooney model, $\eta_r = \exp\{[\eta]\phi/(1 - \phi/\phi_p)\}$; (◇) Eiler model, $\eta_r = \{1 + (1/2)[\eta]\phi/(1 - \phi/\phi_p)\}^2$; (□) Krieger−Dougherty model, $\eta_r = \{1 - \phi/\phi_p\}^{-[\eta]\phi p}$, where η_r is relative viscosity, $[\eta]$ is intrinsic viscosity, and ϕ is volume fraction of the solute. Dendrimer solutions are represented as indicated in the figure.

EDA solutions of the first six generations (i.e., generations 0 through 5) of examined PAMAM dendrimers with the theoretical predictions of three frequently used models of idealized suspensions of "hard-spheres" (i.e., the Krieger-Dougherty,[27] Eiler,[28] and Mooney[29] models, respectively). For this comparison, the respective solution volume fractions were obtained using experimentally determined bulk densities of dendrimers (listed in Table 1),[12] while the theoretical curves were calculated based on the value of 0.0175 P for the viscosity of the EDA solvent.[9]

It can be seen from this figure that although the observed behavior of these dendrimer solutions clearly deviated from that expected for the suspensions of nondraining "hard-spheres" of uniform densities, it was in fact approaching it with an increase in the dendrimer generation. This indicates an increase in the dendrimer nondraining character with generations and is consistent with the experimentally observed decrease of the ratio of dendrimer radius of gyration and hydrodynamic radius (R_g/R_h) from 0.94 for generation 3 to 0.74 for generation 5, as shown in Table 1. The deviation of the generation 5 value from 0.775 that is theoretically expected for idealized nondraining "hard spheres"[30] probably results from dilute solution measurements and may reflect difficulties in the precise determination of intrinsic viscosities of strongly "polyelectrolytic" PAMAM dendrimers.[9] However, despite this reservation, it still seems that the available data support the conclusion that with increase in generation dendrimers tend to develop from "softer", more draining molecules toward "hard", nondraining spheroids. This is consistent with the proposed concept of generationally dependent "closure" (i.e., densification) of the dendrimer outer surface upon its interior, and the resulting dendrimer impenetrability to other dendrimers, their parts, or other large molecules.[31] This is also consistent with the SAXS data which showed hard sphere-type scattering functions for dendrimer generations 5 through 10,[3] as well as with the recent theoretical prediction of the relationship between the dendrimer hydrodynamic radius and the radius of gyration.[32]

However, the observed deviations from idealized "hard-sphere"-type behavior (particularly for lower generations, see Figure 9) are nevertheless considerable enough to indicate that a certain degree of "softness" exists within these dendrimer molecules. This suggests that the source of dendrimer "softness" must be in their interior which, in higher generation dendrimers (i.e., above the CDB), is relatively "spongy" with respect to the surrounding "denser", congested surface, as proposed by the "dense-shell" model for dendrimer *intra*molecular morphology.[12] This type of molecular morphology implies that there must be considerable "cargo space" inside these molecules wherein they can accept small molecular weight solvents or other organic and/or inorganic guests. This can explain numerous experiments which clearly demonstrated unprecedented dendrimer ability to serve as nanoscopic "encapsulators",[33a−b] "boxes",[33c] "containers",[33d−g] or "molecular sponges",[33g,h] and it also agrees with the results of recent SAXS studies which showed that dendrimers act as particles "with rather sharp boundaries".[3] In addition to this, such dendrimer *intra*molecular morphology would also imply their ability to expand on solvation (particularly in good solvents and with increasing solvent power[34]) or with an increase in temperature, as well as to deform at higher solution concentrations or when exposed to external stress. The latter was clearly manifested in this study by the observed independence of dendrimer solution viscosity on repeated loading (see Experimental section).

To avoid potential confusion with various conflicting views that have been expressed in the literature on this subject matter, it is important to note that the "dense-shell" model of dendrimer *intra*molecular morphology does not support or dispute in any way any of the previously proposed theoretical and/or computer-generated ones. Its presentation of a dendrimer molecule results solely from experimentally determined properties of real dendrimers and is, consequently, more descriptive and less elaborate, but perhaps physically realistic. Therefore, it does not imply much about fine details of the dendrimer structure, such as the exact thickness of the dense dendrimer shell at each generation or the exact location of the end-groups (which has been and still is one of the "burning" issues among dendrimer scientists). In fact, it does not require that all end groups must necessarily reside at the outer molecular surface,[35] and it readily permits a certain, generationally dependent amount of "bending back" of the outer segments into the dendrimer interior.[36,37] However, this does not seem likely to occur to a very high extent at higher dendrimer generations and is probably sterically restricted to only few outermost branch cell layers.[38] It can be roughly estimated that the "soft" and "spongy" interior probably does not extend further than only a few (perhaps two to four) generational layers away from the dendrimer core. Thus, in a sense, the "dense-shell" model is between the de

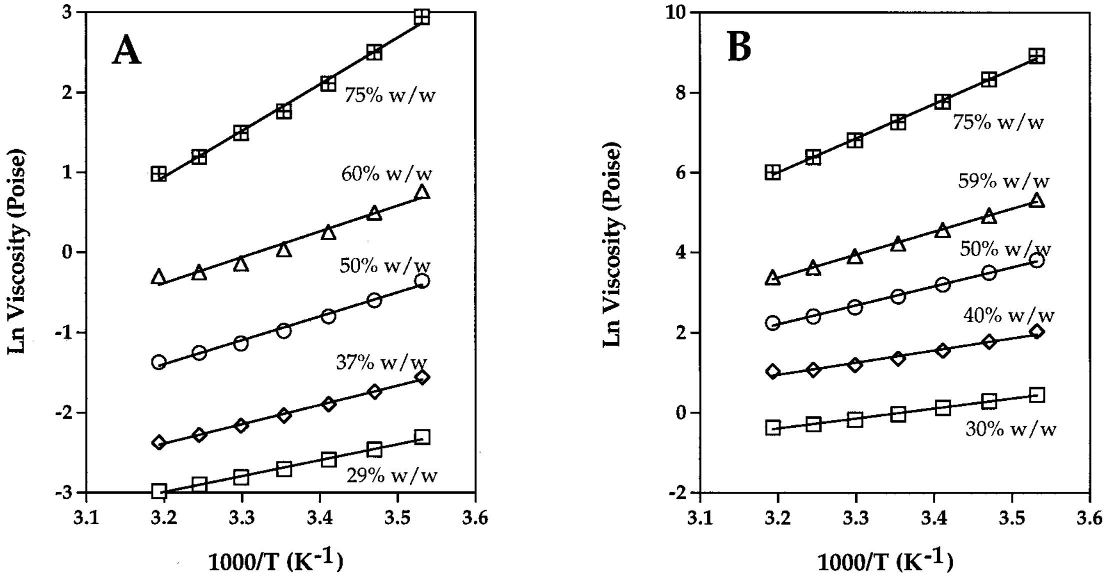


Figure 10. Temperature dependence of the solution viscosities of generations 0 (A) and 6 (B) ethylenediamine (EDA) core–polyamidoamine (PAMAM) dendrimers in ethylenediamine (EDA) solvent at indicated solution concentrations.

Gennes–Harvet “extended arms model”[35] and the Muthukumar–Lescanek kinetic “bending back” model,[36] and it seems to be consistent with the theoretical “density well” model proposed by Mansfield and Klushin,[14] as well as with a number of various experimental observations described or referred to in this work.

Dependence of Dendrimer Solution Viscosity on Temperature. The dependence of dendrimer solution viscosity on temperature is illustrated for generations 0 and 6 in Figure 10, while all numerical values for these and other examined solutions are listed in Table 2.

It can be seen from this figure that within the temperature range studied (i.e., from 10 to 40 °C) these dendrimer solutions exhibited very good linear relationship between ln η and $1/T$, in agreement with the kinetic rate theory of flow as represented by the Arrhenius–Frenkel–Eyring-type equation ($\ln \eta = A + \Delta E_\eta/RT$).[39] This finding is not surprising because (a) the temperature range studied was clearly rather narrow and because (b) in all examined cases it was well above the glass temperatures (T_g) of the respective solutions. As determined by differential scanning calorimetry (DSC) these T_gs depended on dendrimer generations and solution concentrations, and ranged between below −100 °C, for the 50 wt % solution of generation 6 dendrimer and lower concentration solutions of this and lower generation PAMAMs, and −45 °C, for the 75 wt % solutions of generation 5 and 6 dendrimers. Therefore, in all cases the temperature range studied was more than 50 °C above the respective T_g values, so that effects of the proximity of T_g on the flow properties could be considered negligible. On the other hand, the dependence of solution viscosity on dendrimer size and temperature was rather strong (see data of Table 2), indicating that these molecules may undergo considerable deformation with solution concentration and temperature (i.e., exhibit a surprising degree of flexibility and/or pronounced free volume effects). This is clearly consistent with the proposed “soft” and “spongy” character of the dendrimer molecular interior and with their deformability on exposure to external stress.

Activation Energy of Flow of Dendrimer Solutions. The observed linearity of ln η vs $1/T$ relationships of these dendrimer solutions indicates that within the examined temperature range their “apparent” activation energy of flow (E_η) was constant and independent of temperature. Therefore, the E_η values could be calculated from the slopes of these relationships to give the dependence of E_η on dendrimer solution concentration, as shown in Figure 11.

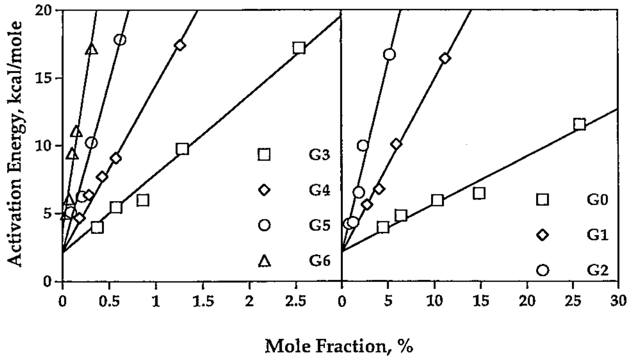


Figure 11. Activation energy of steady shear flow as a function of dendrimer molar fraction for ethylenediamine (EDA) solutions of ethylenediamine (EDA) core-polyamidoamine (PAMAM) dendrimers of indicated generations (G) within the temperature range 10–40 °C.

It can be seen from this figure that the obtained dependence was linear in all cases (i.e., for all dendrimer generations) and that all lines had a common origin at 0% dendrimer concentration. This intercept gives about 2.6 kcal/mol for the activation energy of flow of pure ethylenediamine solvent, which seems quite reasonable since for most solvents E_η is usually between 1.5 and 3.5 kcal/mol.[40] On the other hand, this linear dependence of E_η on concentration differs from the corresponding relationships that are typically found for the solutions of linear and/or randomly branched chain polymers, where a break in E_η vs c slope is normally observed.[41] Since the appearance of this break may be associated with establishment of entanglement couplings,[42] the observed linearity of E_η vs c in dendrimer solutions seems to represent yet another manifestation of dendrimer impenetrability to other dendrimers or their parts.

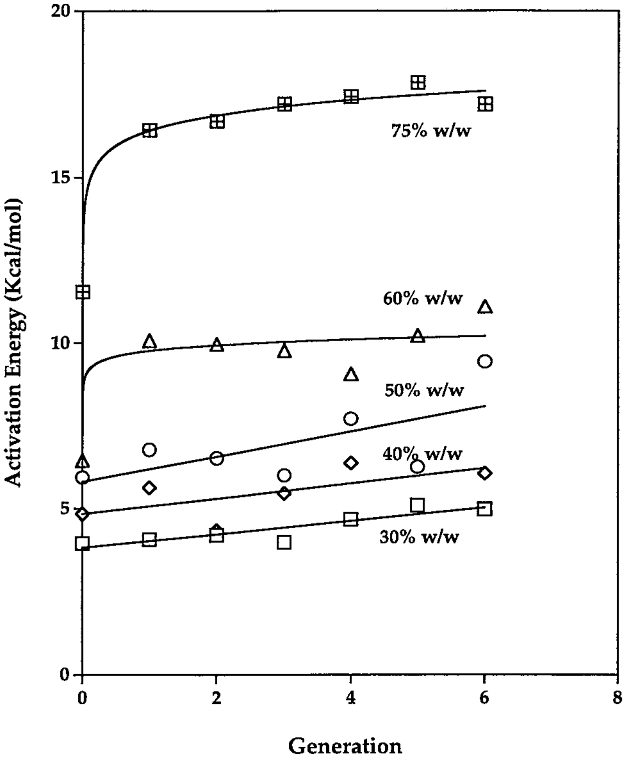


Figure 12. Activation energy of steady shear flow as a function of generation for ethylenediamine (EDA) solutions of ethylenediamine (EDA) core–polyamidoamine (PAMAM) dendrimers of indicated concentrations.

In addition to this, the steep increase of activation energy of flow with solution concentration observed for practically all dendrimer generations studied (see Figure 11) is consistent with what would be expected for polymers that have large number of polar groups, rheologically semirigid segments and high degree of regular branching. However, the fact that there are no breaks in the slopes of E_η vs c relationships indicates that there is only one type of rheological unit involved in the dendrimer flow. Consequently, this seems to suggest that entire dendrimer molecule constitutes this individual rheological unit (i.e., that dendrimer flow occurs predominantly through “molecular” level motions).

Figure 12 shows dependence of the apparent activation energy of flow on the dendrimer generation (i.e., molecular weight). It can be seen from this figure that with increase in concentration, E_η increased with molecular weight at lower generations, but relatively quickly reached a plateau value at about generation 2 or 3. This may be associated with the onset of “closure” of outer dendrimer surface above the critical degree of branching (CDB) stage and with the consequent reduction of *inter*molecular hydrogen bonding, which would be expected to result in the observed decrease in the rate of E_η change with generation.

Conclusions

The results obtained in this study show that dendrimers exhibit highly specific shear flow behavior which is unprecedented among the high molecular weight polymers and appears to be solely driven by their unique macromolecular architecture. In particular, this behavior includes the following main features. First, the flow of dendrimer solutions appears to be perfectly Newtonian even at very high molecular weights and solution concentrations. Second, both in solutions and in the bulk state, dendrimers exhibit characteristic viscosity vs molecular weight relationships which seem to be independent of their chemical composition and clearly and significantly different from both high molecular weight chain-type polymers and suspensions of idealized spherical particles. Third, the pronounced susceptibility of dendrimer solution viscosity to temperature indicates that these macromolecules exhibit a surprising degree of inherent flexibility. Fourth, dendrimer solution viscosities are independent of repeating loading, and fifth, the dependence of the activation energy of flow of dendrimer solutions on dendrimer size (i.e., generation) indicates that their entire molecules represent the smallest rheological units involved in that flow.

From these features, it seems that the following conclusions can be drawn about the physical nature of dendrimer molecules and their interactions. First, they indicate that fully developed dendrimers do not engage in *inter*dendrimer interactions, which, in turn, suggests that their outer molecular surfaces are impenetrable to other dendrimers, their parts, or other large molecules. This has been also confirmed by the results of small-angle X-ray scattering studies which showed no interference resulting from *inter*dendrimer correlations,[3] and it is consistent with the demonstrated entrapment of linear macromolecules prepared in the “confined environment” of the dendrimer molecular interior.[31] Furthermore, this conclusion is also supported by the molecular modeling studies and dendrimer structural analysis performed in this work, which indicate that the molecular reason responsible for this dendrimer property is the “closure” (or “densification”) of the dendrimer outer surface, which occurs above a certain generation that is related to the critical degree of branching (CDB).

Second, the dependence of dendrimer solution viscosity on concentration shows that while these molecules resemble “soft” (partially draining) spheroids, their “hardness” increases with generation. Combined with the observed dendrimer ability to expand on solvation,[9,12,34] this “softness” seems to originate from the interior of their molecules. It may also be a probable reason for the somewhat surprising dendrimer flexibility, as manifested by the pronounced sensitivity of the solution viscosities to temperature. Conversely, the stability of dendrimer solutions to repeated loading suggests that dendrimers possess an appreciable ability to deform under stress, probably through a high degree of cooperation between their interior segments. This *intra*molecular segmental cooperativity may also explain why entire dendrimer molecules appear to act as individual rheological units in the flow of dendrimer solutions.

On the basis of these results and conclusions, it is proposed that the architecturally unique dendrimer molecules behave as if consisting of a “soft” and “spongy” interior surrounded by a well-defined “dense” outer shell.[12] While this shell imparts dendrimer impenetrability to other dendrimers or large molecules and the absence of *inter*dendrimer interactions, as reflected through Newtonian flow behavior and specific viscosity–molecular weight relationships, the interior provides a “cargo space” which can accommodate solvent molecules or other small molecular weight organic or inorganic “guests”. It is also proposed that Newtonian flow behavior and the absence of *inter*dendrimer interpenetration may represent distinguishing "fingerprint" properties characteristic of all fully developed dendrimers, which set them apart from all other known classes of macromolecular architecture.[26] Fully developed dendrimers may be defined by the critical degree of branching (CDB) which may serve as a criterion for distinguishing dendrimers from their lower molecular weight, simple branched precursors.

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