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# The Melt Viscosity of Dendritic Poly(benzyl ether) Macromolecules

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ABSTRACT: The zero shear melt viscosity, $\eta_0$, for a variety of dendritic poly(benzyl ether) macromolecules has been measured. The viscosity of low generation dendrimers exhibits a strong molecular mass, $M$, dependence, yet, direct proportionality between $\eta_0$ and $M$ is observed at higher generations. The viscosity scales with $M$ for mono- and tridendrons rather than generation number. Hypercore dendrimers continue this scaling although the viscosity is slightly greater. A large deviation from the master curve for the mono- and tridendrons is found for an end-substituted monodendron. The viscosity for the end-substituted monodendron is also much more temperature dependent than virgin dendrimers, and it is concluded that end groups have a much larger effect on the viscosity than the core. Reexamination of literature data for intrinsic viscosity and glass transition temperature is performed, and these quantities also scale with molecular mass. Comparison with free volume theory indicates that the theory is extremely robust although some question of its validity is made when applied to dendrimers.

## Introduction

Dendritic macromolecules are a new and promising class of synthetic polymers. These molecules have a "tree-like" structure, with branches emanating from a multifunctional core and from each unit of monomer. The molecular mass approximately doubles at each generation of dendritic growth, thus, the chain ends contribute about one-half of the mass irrespective of the degree of polymerization. Consequently, this compact architecture is not only of great novelty but promises great utility, and applications as diverse as drug delivery and lubrication have been discussed in the literature.[1]

Several theoretical structural descriptions of dendritic macromolecules have been reported. The first, the statistical treatment of de Gennes and Hervert,[2] anticipated that "ideal" dendritic growth could not occur indefinitely because the mass increases exponentially with generation whereas the volume only increases cubically. This work indicated the periphery of the molecule must become increasingly crowded as polymerization continues, ultimately prohibiting further dendritic growth.

An alternate description emerged from computational studies. Computer-assisted molecular modeling experiments suggested that Starburst PAMAM dendrimers proceed through a continuum of morphologies as the generation is increased.[3] Open, hemispherical structures were favored at low generation, but the simulations suggested closed spheroids, with well-developed hollows, were formed at higher degrees of polymerization.

Lescanec and Muthukumar[4] used a kinetic model to determine how the density and radius of gyration changed during dendritic growth. This work, although focused on unequilibrated structures, indicated the chain ends may be "buried" within the dendritic macromolecule, a point overlooked in the treatment by de Gennes and Hervert.[2] A markedly different density profile results from this distribution of chain ends, and the relationship between the radius of gyration and molecular mass is quite unlike that observed for linear macromolecules. The simulation showed the radius of gyration is proportional to $M^{0.5}$ at low molecular mass ($M$) and $M^{0.22}$ at high molecular mass. Consequently, these workers predicted an unprecedented, bell-shaped relationship between the intrinsic viscosity and the molecular mass.

Mansfield and Klushin[5] applied a Monte Carlo method to the simulation of the conformation of dendritic macromolecules. This method differed from the kinetic growth approach because the "molecules" were allowed to attain an equilibrium configuration judged by a constant radius of gyration. Nevertheless, the conclusions drawn from the work were similar to those of Lescanec and Muthukumar.[4] The simulation suggested the chain ends were not localized to the periphery of the molecule, and it was asserted that all regions of the molecule, including the surface, were saturated with end groups. Some evidence of hollowness within the molecules was also demonstrated, and it was concluded that the extent of backfolding was insufficient to fill the void space. Subsequent work indicated the branches of Starburst dendrimers are not well mixed, therefore, the void space may arise as an artifact of the assumption of spherical symmetry.[6]

Murat and Grest[7] explored the effect of solvent quality on the structure of dendrimers by off-lattice molecular dynamics simulation. This work suggested the radius of gyration scaled with the cube root of the degree of polymerization irrespective of the solvent power and dendrimers are compact structures, with uniform, scale-independent densities. Significantly, this work sug-

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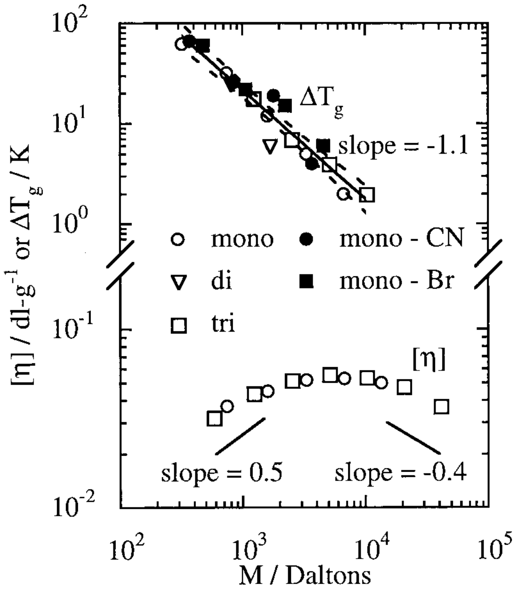

**Figure 1.** The intrinsic viscosity and $\Delta T_g$ of dendritic poly(benzyl ether) versus molecular mass. The data are from Mourey et al.[9] and Wooley et al.[13] Key: (open circles) monodendrons; (open triangles) didendrons; (open squares) tridendrons; (filled circles) monodendrons end-substituted with CN; and (filled squares) monodendrons end-substituted with Br. Limiting slopes of 0.5 and −0.4 for the intrinsic viscosity with molecular mass are also shown (see text for details). The solid line represents the linear regression and the dashed lines are the 95% confidence limits for $\Delta T_g$ with $M$.

gested the monomers belonging to generations zero to four are localized at increasing radii, as envisaged in the earliest statistical treatment of dendrimer structure. However, the monomers of subsequent generations appear to saturate the entire molecule. Perhaps the most exciting implications of this work concern the dynamics of structural reorganization. It was demonstrated that the relaxation time derived from the autocorrelation function of the radius of gyration is clearly influenced by the solvent power, but is not a simple function of the generation number. The authors conceded this behavior may reflect some computational inefficiency yet suggested structural relaxation may be complicated by the extent of entanglement between different branches of the molecule, irrespective of the generation.

It is difficult to question the validity of these theoretical concepts without physical measurements of the materials. To date, these measurements have been limited by the scarcity of well-characterized material. However, two notable exceptions are the intrinsic viscosity and the thermal properties.

Preliminary work with unsymmetrical poly(lysine) cascade molecules indicated the intrinsic viscosity ($[\eta]$) was essentially independent of the molecular mass.[8] This behavior was easily reconciled with predictions of a closed, nondraining, spheroidal architecture. The examination of a series of high molecular mass dendrimers, in later work, caused a marked change in this understanding. The data for a series of dendritic poly(benzyl ether) macromolecules measured by Mourey et al.[9] are shown in Figure 1. The data have been replotted here as intrinsic viscosity versus molecular mass rather than generation number. Interestingly, the two different types of dendrimers, monodendrons and tridendrons, show very similar behavior, and the maximum in the intrinsic viscosity occurs at the same molecular mass (≈ 4000 Da). This result may indicate the polymer configuration for these two types of polymers is very similar for a given molecular mass.

As mentioned by Mourey et al.,[9] the data convincingly indicate that some form of structural reorganization takes place as the dendrimers increase in size. Similar data have been collected for dendritic PAMAN[1] and poly(trimethylene-imine)[11] systems, lending further support to the concept of high molecular mass dendrimers not as closed spheroids, but as flexible globular structures.[12] Also, the intrinsic viscosity—molecular mass limiting slope predictions of Lescanec and Muthukumar[4] agree fairly well with the intrinsic viscosity data as shown in the figure.

Further insight into the structure of these molecules was achieved through investigation of their thermal properties. The glass transition for a variety of dendritic materials has been examined by differential scanning calorimetry (DSC). Wooley et al.[13] reported the relationship between the glass transition temperature ($T_g$) and the molecular structure for dendritic poly(benzyl-ether) macromolecules. This work demonstrated the relationship between $T_g$ and the molecular mass is not unlike that of linear molecules (i.e., $T_g$ increases with mass to a limiting value at high molecular mass). The authors modified conventional theory, which associates the molecular mass dependence of $T_g$ with the relative influence of the free volume at each chain end, to account for the large number of terminal (or end) groups ($N_E$) in these macromolecules

$$\Delta T_g = \frac{k}{M} \qquad \text{(linear)} \tag{1}$$

$$\Delta T_g = \hat{k}\left\{\frac{N_E}{M} - \frac{N_E}{M}\bigg|_\infty\right\} \qquad \text{(dendrimer)} \tag{2}$$

where eq 1 is for linear molecules and eq 2 is for dendrimers; $\Delta T_g$ is the glass transition temperature in the limit of infinite molecular mass ($T_{g\infty}$) less that for a given mass, $k$ and $\hat{k}$ are constants related to the free volume of an "end," and the subscript ∞ means "evaluated at infinite molecular mass". Note, because linear polymers only have two ends, the influence of the ends tends to zero at infinite molecular mass. However, the influence of the ends for dendritic macromolecules has a finite limit at infinite molecular mass because $N_E/M$ approaches a finite non-zero limit. For example, the limit is 0.00472 Da$^{-1}$ for the dendrimers used here and by Mourey et al.[9] By comparison, $N_E/M$ is of the order 0.006 Da$^{-1}$ for lower generation dendrimers.

The influence of the chain-ends on the glass transition was conclusively demonstrated by comparing the behavior of structural analogues that differed only at their terminal groups. Dendrimers with different terminal substituents had limiting values of $T_g$ that varied by almost 50 K. Similar observations have recently been made with dendritic poly(trimethylene-imine).[11]

Kim and Beckerbauer[14] investigated the role of end groups on the glass transition of hyperbranched polyphenylene and analogous triphenylbenzene derivatives. The correlation of the substituent effect in the hyperbranched molecules and the small molecule analogues led these authors to conclude the main relaxation mode of the glass transition in the hyperbranched and the small molecules are likewise correlated. Thus, these authors proposed relaxation occurs through translational motion of the molecule rather than segmental chain motion.

Stutz and co-workers[15,16] have utilized glass transition theory for cross-linked polymers to arrive at a relation for $T_g$ as a function of molecular mass for dendrimers. We have modified this theory to arrive at the following form (see the *Appendix*)

$$\Delta T_g = \frac{\hat{k}_1}{N_b^g - 1} + \frac{\hat{k}_2}{N_b^{g-1}} \tag{3}$$

$$\hat{k}_1 = k_1 \frac{N_c + C}{N_c[N_b + 1]} \{N_b - 1 + k_2\} \tag{4}$$

$$\hat{k}_2 = k_2 \left\{ \frac{T_g^\infty}{N_b - 1} - k_1 \frac{N_c N_b^g + C}{N_c[N_b^g - 1][N_b + 1]} \right\} \tag{5}$$

where $k_1$ and $k_2$ are constants related to the end groups and branch points, respectively, $N_c$ represents the core multiplicity (e.g., one for monodendrons, two for didendrons,...), $N_b$ is the branch multiplicity (two for the dendrimers used here, the functionality of the dendrimers is $N_b + 1$), $g$ is the generation number, $C$ is a constant that is one for monodendrons to account for the end from the core and zero otherwise, and $T_g^\infty$ is the glass transition temperature for an equivalent linear polymer in the limit of infinite molecular mass. The modification we have made is to include $C$ in the total number of ends in the molecule (i.e., Stutz uses $N_c N_b^g$ and we use $N_c N_b^g + C$). This modification has a significant effect as described later.

Note that eq 3 reduces to eq 1 because $k_2$ is identically zero and $N_b$ is one for linear polymers ($g$ becomes the degree of polymerization for linear polymers, l′Hôpital's must be used in the limit of $N_b \rightarrow 1$). Also, eq 3 is equivalent to eq 2 when $k_2$ is taken as zero and the molecular mass contribution from the core and terminal groups (ends) in eq 2 are neglected.

We found it difficult to fit the data utilizing a nonzero value of $k_2$, even when $C$ is set equal to zero as in Stutz's original theory.[16] The effect of $C$ on prediction of $\Delta T_g$ is substantial. For example, taking $k_2$ equal to zero, it is easy to determine that $\hat{k}_1$ for monodendrons is two times that for di- and tridendrons assuming $k_1$ is a fundamental constant. In fact, by fitting $\Delta T_g$ to eq 3, one finds $\hat{k}_1$ is 76 ± 15 *K* for monodendrons and 23 ± 5 *K* for di- and tridendrons using the data from ref 13. The ratio of these two constants is 3.3 ± 1.0, which is not equal to the expected value of 2, and a different model for the change of the glass transition temperature with molecular mass is given in eq 6. (Note $T_\infty$ values of Wooley et al.[13] were used.)

Taking $k_2$ equal to zero in eq 3 is approximately equivalent to correlating $\Delta T_g$ with $1/M$. This correlation is tested in Figure 1, and a linear relation is almost obtained with $\Delta T_g$ proportional to $1/M^{1.1}$, regardless of the dendrimer type. The effect of end-substituted monodendrons is also given in the figure, and they too fall onto the master curve. This result occurs despite the fact that $T_{g\infty}$ is 14 and 36 *K* higher for the two end-substituted monodendrons considered.[13] This correlation suggests the following form for $\Delta T_g$

$$\Delta T_g = T_c \frac{m_c}{M} \tag{6}$$

where $T_c$ is a characteristic temperature and $m_c$ is a characteristic molecular mass. The characteristic temperature may be taken as the ratio of the interaction energy between neighboring segments ($E_0$), to Boltzmann's constant ($k_B$) or some function thereof,[17] the inverse of the thermal expansion coefficient, or some other physical quantity with dimensions of temperature.

Assuming $\Delta T_g$ is proportional to $1/M$ ($\Delta T_g M = 2.2 \times 10^4 \pm 29\%$ K-Da), one can determine from the data that $m_c$ is ~70 Da, which is smaller than the molecular mass of a branch unit (121 Da). The aforementioned value of $m_c$ was determined by taking $T_c$ equal to $T_{g\infty}$ (~320 *K*), which was found by Gibbs and DiMarzio[17] to be approximately equal to $E_0/k_B$. Were the inverse of the thermal expansion coefficient for the free volume used (≈1000 *K* as found later), then $m_c$ is 20 Da. Both these values are less than the molecular mass of a "monomer" unit; thus, the change in $T_g$ with molecular mass for dendrimers is possibly due to small scale motions.

We realize the implication that $m_c$ is the mass of the effective glass "unit" is somewhat controversial, especially when it is smaller than the monomer size. Pietralla et al.[18] used the relation determined by Heuer and Speiss[19] to find the mass of an effective glass unit is on the order of five times smaller than the monomer size. Their unit is related to the absolute value of the glass transition temperature (i.e., $T_{g\infty}$), whereas we are defining a unit based on the change of $T_g$ with molecular mass. We do not comment further on the magnitude of $m_c$ and merely note that eq 6 can be interpreted in a manner similar to eqs 1 and 2 if $m_c$ is considered as related to the "free volume" of the ends . Yet, we have not invoked any special significance to $m_c$ as a factor related to the ends. Indeed, the change of the glass transition temperature with molecular mass appears to be independent of end type. The end type does, of course, have an effect on $T_{g\infty}$.

Our suggestion, based on the empirical plot in Figure 1 and eq 6, is that the glass transition temperature is composed of two components: one component is related to end-group substitution and affects the value of $T_{g\infty}$, whereas the other is related to a characteristic molecular mass. This suggestion is similar, in principle, to Stutz's[16] proposal where he developed a relation with separate end-group and branch-point contributions to $T_g$.

A note of caution: for a given molecular mass one can easily determine the number of ends is essentially the same for di- and tridendrons, whereas there is approximately one extra end for a monodendron. Thus, a master curve, such as that given in Figure 1, can also be obtained by plotting $\Delta T_g$ versus the number of ends per molecule (within experimental error). This idea does not, however, explain the superposition of the data of the chain-end-modified monodendrons that fall onto the master curve if chain ends are considered as the dominant factor for a change in $T_g$.

The purpose of the discussion just presented on the intrinsic viscosity and glass transition temperature is to highlight the apparent simplistic behavior of dendrimers provided both quantities are related to the total molecular mass. It has already been demonstrated that the melt viscosity of mono- and tridendrons fall on a master curve if correlated with molecular mass.[20]

In this work, a detailed analysis of the melt viscosity for dendritic macromolecules based on benzyl-ether is presented. The original work of Hawker et al.[20] is expanded upon and the temperature dependence of the viscosity is determined. In addition, a hypercore system and the effect of terminal groups on a monodendron are considered. We examine these data in the context of contemporary theory and consider the implications on the structure and dynamics of dendritic molecules. Also, given the results of the aforementioned empirical correlations (cf., Figure 1) we want to determine how the melt viscosity is affected by the plethora of end groups in a dendritic polymer. Details may be found in Farrington.[21]

## Theory

Using the Rouse theory, to first order, the melt terminal viscosity ($\eta_0$) of simple, linear polymers increases in direct proportion to the molecular mass, at least until the onset of entanglement coupling (see e.g., Ferry[22]). This behavior is traditionally described by a relationship involving Avogadros number ($N_A$), the melt bulk density ($\rho$), the monomer step length ($L_m$) and mass ($m_o$), the monomeric friction coefficient ($\zeta_o$), and the molecular mass of the molecule

$$\eta_0 = \frac{N_A \rho L_m^{\ 2}}{36 m_o^{\ 2}} \zeta_o M \qquad (7)$$

It has been observed many times that a plot of the zero shear viscosity against molecular mass of short-chain polymers is rarely linear because the density and the monomeric friction coefficient are themselves functions of the molecular mass. Hence, the apparent simplicity of the relation in eq 7 is only preserved under certain conditions. Allen and Fox[23] satisfied these conditions by preparing binary blends of monodisperse poly(styrene) with a constant density of chain ends. These authors varied the weight average molecular mass ($M_w$) of the blends but held the number average molecular mass and, therefore, the number of chain ends in the sample constant. This work showed direct proportionality is observed between $\eta_0$ and $M_w$ under these conditions, and clearly associated the macroscopic density of low molecular mass, linear polymers with the concentration of chain ends in the sample. Extensive discussion of the aforementioned results are given in Berry and Fox[24] as well as Ferry.[22]

Williams et al.[25] developed a theory (now denoted as WLF theory) to describe the temperature dependence of rheological properties near the glass transition temperature. These authors argued that free volume plays a major role in the opposing forces experienced by the units involved in motion, and markedly affects properties near the glass transition temperature. The shift factor ($a_T$) for the ratio of relaxation times (which under most conditions is equivalent to the ratio of viscosities) at a given temperature ($T$) to a reference temperature ($T_o$) is given by

$$\log_{10} a_T = -\frac{C_1(T - T_o)}{C_2 + T - T_o} \qquad (8)$$

where $C_1$ and $C_2$ are fitting constants that have physical meaning according to the WLF theory. Utilizing standard relations in the theory, one can determine the fractional free volume at the glass transition temperature ($f_g$), the fractional free volume thermal expansion coefficient ($\alpha_f$) and the viscosity at the glass transition

$$f_g = \frac{B}{\tilde{C}_1}\left[1 + \frac{T_g - T_o}{C_2}\right] \qquad (9)$$

$$\alpha_f = \frac{B}{\tilde{C}_1 C_2} \qquad (10)$$

$$\eta_0(f_g) = \eta_0(f_o)\exp\left(\tilde{C}_1\left[\frac{f_o}{f_g} - 1\right]\right) \qquad (11)$$

where $B$ is a constant usually taken as unity, $\tilde{C}_1$ is ln 10 × $C_1$, and $f_o$ is the fractional free volume at the reference temperature ($B/\tilde{C}_1$).[22]

The value of $f_g$ has been found to be ~0.025 for many polymers, although this may not necessarily be taken as a universal parameter.[22] The viscosity at the glass transition, determined with eq 11, is typically $10^{12}$ Pa s, although Fox and Flory[26,27] found a molecular mass dependence for polystyrene fractions. The value of $\eta_0(f_g)$ was constant and equal to ~109 Pa s at low molecular mass (as low as 3000 Da where $T_g$ was equal to 43 °C, compared with 100 °C for $T_g$ at large molecular mass) then increased above the critical molecular mass ($M_c$) for entanglements ($M_c \approx 35\,000$ Da) to order 1012 Pa s and higher. However, an interesting point not usually mentioned is that $\eta_0(f_g)$ shows a shallow minimum at a molecular mass of 7000 Da. This observation will be discussed later.

One can also use eq 11 to determine the viscosity at a constant fractional free volume, by using an assumed value of $f$ rather than $f_g$. This assumed value is used to compare the viscosity for a series of molecular masses in an “iso-free volume” state.[28,29] When this is done, the viscosity is typically a linear function of the molecular mass at low molecular mass (i.e., below the characteristic molecular mass for entanglements).

## Experimental Section

Dendritic poly(benzyl-ether) macromolecules, based on 3,5 dihydroxybenzyl alcohol, were used in this study. These macromolecules were prepared by the convergent growth approach, where the synthesis begins at the terminal groups and culminates with the attachment of dendritic fragments (dendrons) to a multifunctional core molecule. As a consequence of this synthetic strategy, the molecular mass of the product is almost exactly defined and well controlled.

Three series of dendrimers were investigated in this work. Monodendrons were formed to six generations by convergent growth.[29] Samples of these materials were attached to 1,1,1-(4′-hydroxyphenyl)ethane core molecules to form tridendrons. Likewise, samples of the fourth generation monodendron (denoted as [G-4]—OH) were attached to dendritic cores to produce hypercore macromolecules[30] where up to 24 monodendrons were attached to the hypercore (denoted as, for example, $[G\text{-}4]_6$—[val.C], where the subscript 6 denotes six monodendrons). The physical properties of these materials were explored in earlier work[13] and are summarized in Table 1. In addition, the rheological properties of a single-end-substituted monodendron were investigated. The terminal (or end) groups of a fourth generation monodendron were substituted with a methylester group as shown in the table.

Samples (~25 mg) of the monodendrons, tridendrons, and dendritic hypercores were compression molded into thin disks (0.5 to 1 mm) under reduced pressure at 5° above the glass transition temperature of each material. Clear disks were obtained from all the polymers except for [G-1]—OH, [G-2]—OH, and $[G\text{-}0]_3$—[C]. These samples recrystallized after molding and formed opaque, white disks. The melt viscoelastic properties of the materials were measured using a modified

**Table 1. Physical Properties of Dendrimers Used in his Study**[a]

| dendrimer | $M$, Da | chain ends | $T_g$, K |
|---|---|---|---|
| | Monodendron | | |
| [G-1]—OH | 320 | 3 | 255 |
| [G-2]—OH | 744 | 5 | 285 |
| [G-3]—OH | 1592 | 9 | 305 |
| [G-4]—OH | 3288 | 17 | 312 |
| [G-5]—OH | 6680 | 33 | 315 |
| [G-6]—OH | 13464 | 65 | 316 |
| | End-Substituted Monodendron | | |
| $(E)_{16}$—[G-4]—OH[b] | 4216 | 17 | 331 |
| | Tridendron | | |
| $[G\text{-}0]_3$—[C] | 576 | 3 | 282 |
| $[G\text{-}1]_3$—[C] | 1212 | 6 | 298 |
| $[G\text{-}2]_3$—[C] | 2484 | 12 | 309 |
| $[G\text{-}3]_3$—[C] | 5026 | 24 | 312 |
| $[G\text{-}4]_3$—[C] | 10126 | 48 | 314 |
| $[G\text{-}5]_3$—[C] | 20292 | 96 | 315 |
| | Hypercore | | |
| $[G\text{-}4]_6$—[val.C] | 20712 | 96 | 322 |
| $[G\text{-}4]_{12}$—[val.C] | 41881 | 192 | 320 |
| $[G\text{-}4]_{24}$—[val.C] | 84219 | 384 | 321 |

[a] Data from Wooley et al.[13] [b] E Represents the end group $CH_3O_2C$—.

Rheometrics Fluids Spectrometer (RFS) fitted with 7.9-mm diameter parallel plates. Oscillatory shear experiments were performed within the linear viscoelastic region, at frequencies between 0.1 and 100 rad/s. The sample temperature was set between 60 and 120 °C, and controlled to within 1 °C of the set point. Nitrogen gas was used to force convection within the rheometer oven and to prevent thermal oxidation of the samples.

## Results and Discussion

**Mono- and Tridendrons.** The complex viscosity in the linear viscoelastic region was independent of the frequency for all lower generation mono- and tridendrons, and a slight decrease in the complex viscosity was found for higher generation dendrimers at frequencies approaching the upper frequency utilized in this work. We are concerned with the "zero shear" or terminal viscosity here and only the limiting viscosity is needed. Some representative runs on samples demonstrated the terminal complex viscosity was identical to the terminal viscosity under steady shear.

Hawker et al.[20] found the viscosity of mono- and tridendrons yielded a master curve when the viscosity was plotted against molecular mass rather than generation number. Here, this work is extended to determine the temperature dependence of the viscosity. An example for monodendron melts is given in Figure 2 where a plot of the terminal viscosity, $\eta_0$, against temperature is given (the shift factor is taken as the ratio of the viscosity at a given temperature to that at the reference temperature, $T_o$, of 80 °C = 353 K).

The results were fitted to the WLF equation (eq 8), and the associated parameters, determined from eqs 9 and 10, are given in Table 2. The fits show reasonable agreement with the data indicating this theory may be realistic in predicting the viscosity of the dendrimers. Interestingly, all the parameters in Table 2 agree reasonably well with those for linear polymers.[22] The fractional free volume (divided by $B$) at $T_g$ is independent of dendrimer type and is ~0.032. For example, the "universal" value of $f_g/B$ for linear polymers is taken as 0.025. In addition, $f_g/B$ is independent of the dendrimer (and end group) type, in agreement with Fox and Flory's supposition that the glass transition represents an iso-free volume state.

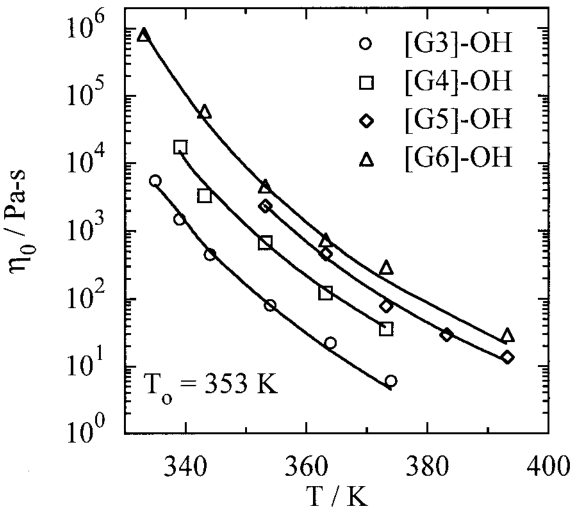

**Figure 2.** The terminal viscosity for various generation monodendrons versus temperature ($T_o$ = 353 K). The curves are the WLF fits of the terminal viscosity using eq 8 assuming $a_T$ is the ratio of viscosities at a given temperature to that at the reference temperature. The WLF parameters are given in Table 2.

**Table 2. WLF Fit and Associated Parameters for the Dendrimers Used in This Study**[a]

| dendrimer | $C_1$ | $C_2$, K | $f_o/B$ | $f_g/B$ | $\alpha_f/B \times 10^4$ K |
|---|---|---|---|---|---|
| | | Monodendron | | | |
| [G-3]—OH | 6.68 | 89 | 0.065 | 0.030 | 7.3 |
| [G-4]—OH | 6.80 | 88 | 0.064 | 0.034 | 7.3 |
| [G-5]—OH | 7.14 | 84 | 0.061 | 0.033 | 7.2 |
| [G-6]—OH | 7.19 | 83 | 0.060 | 0.034 | 7.3 |
| | | End-Substituted Monodendron | | | |
| $(E)_{16}$—[G-4]—OH[b] | 8.93 | 57 | 0.049 | 0.030 | 8.5 |
| | | Tridendron | | | |
| $[G\text{-}1]_3$—[C] | 6.33 | 95 | 0.069 | 0.029 | 7.2 |
| $[G\text{-}2]_3$—[C] | 6.77 | 89 | 0.064 | 0.032 | 7.2 |
| $[G\text{-}3]_3$—[C] | 7.16 | 84 | 0.061 | 0.031 | 7.2 |
| $[G\text{-}4]_3$—[C] | 7.25 | 83 | 0.060 | 0.031 | 7.1 |
| $[G\text{-}5]_3$—[C] | 7.32 | 82 | 0.059 | 0.032 | 7.2 |
| | | Hypercore | | | |
| $[G\text{-}4]_6$—[val.C]<br>$[G\text{-}4]_{12}$—[val.C]<br>$[G\text{-}4]_{24}$—[val.C] | 7.58 | 71 | 0.057 | 0.032 | 8.1 |
| average[c] | | | | 0.032 ± 0.002 | 7.2 ± 0.1 |

[a] $T_o$ = 353 K. [b] $E$ represents the end group, $CH_3O_2C$—. [c] The average is the average for the mono- and tridendrons.

Note the value of $\alpha_f/B$ is equal to 7.2 $\times 10^{-4}$ $K^{-1}$ for the mono- and tridendrons, suggesting a universal value for these dendrimers. This value is not exceptionally large or small when compared with linear polymers and is an intermediate value.[22]

The molecular mass dependence of the fractional free volume is usually taken as

$$f_o = f_\infty + A/M \qquad (12)$$

where $A$ is a constant related to the number of ends per molecule and the free volume for an end.[22] Dendritic polymers have an ever increasing number of ends, $N_E$, with molecular mass, where ultimately $N_E/M$ reaches a constant value as already mentioned. If the $f_o$ data are plotted versus $N_E/M$, a master curve is not obtained. It was already demonstrated that the intrinsic viscosity, $\Delta T_g$, and terminal viscosity all scaled with the molecular

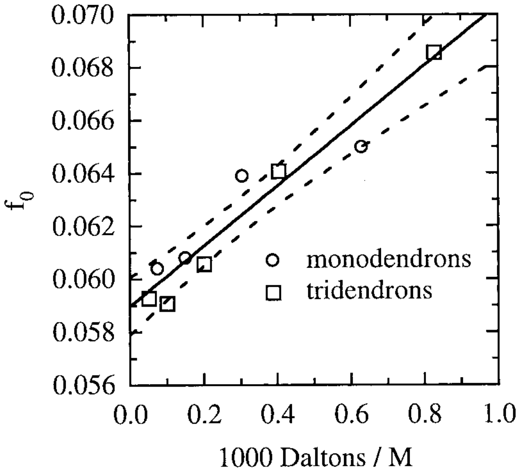

**Figure 3.** The fractional free volume at the reference temperature (353 K) versus inverse of molecular mass for mono- and tridendrons. The solid line is a linear regression and the dashed lines are the 95% confidence intervals.

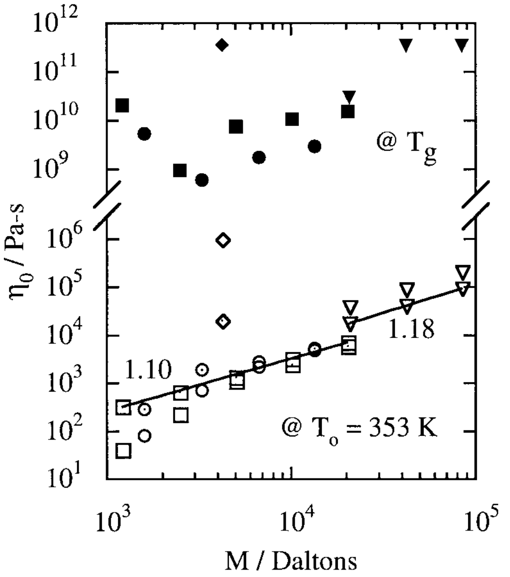

**Figure 4.** The terminal viscosity versus molecular mass for monodendrons (circles), tridendrons (squares), end-substituted [G-4]—OH (diamond), and hypercores (triangles). Open symbols are data at 353 K, dotted symbols are at a constant fractional free volume of 0.06, and filled symbols are at $T_g$. The linear regression for mono- and tridendrons has a slope of 1.10 and for hypercores has a slope of 1.18.

mass. This scaling is checked for the fractional free volume in Figure 3 and a master curve is obtained. In fact, a linear regression seems justified with $f_\infty$ and $A$ equal to 0.059 and 11.4 Da, respectively. This result indicates the constant $A$ is perhaps not related to ends and the free volume theory derivation of eq 12 is flawed when applied to dendrimers. Note that $A$ is of the same magnitude as $m_c$ already given; this fact is merely drawn to the reader's attention and no explanation is given here.

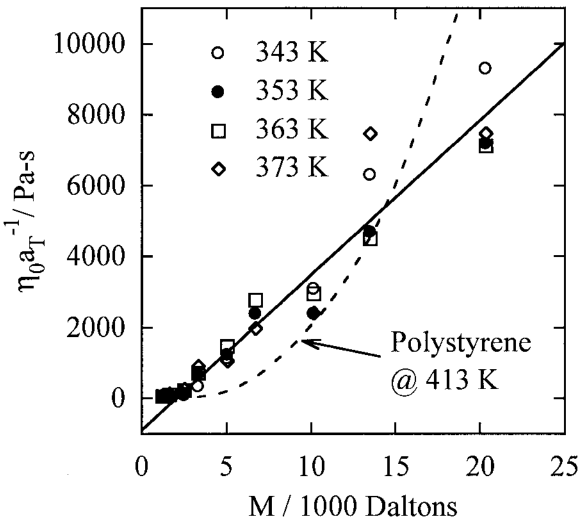

**Figure 5.** The viscosity versus molecular mass on linear coordinates for the monodendrons and tridendrons shifted with the WLF theory. The dashed curve is Fox and Flory's[26,27] data for linear polystyrene at 413 K where the limiting fractional free volume is approximately equal to the limiting value for the dendrimers.

Despite free volume theory (perhaps) being flawed or too robust in its applicability to dendrimers, we present corrections to the terminal viscosity to constant fractional free volume in Figure 4 by using eq 11, where a reference fractional free volume of 0.06 was chosen. This value is close to $f_\infty$ (0.059) determined with eq 12. A power law slope of 1.10 is found for the mono- and tridendrons, which is not affected were $f_\infty$ used. This slope is close to the Rouse prediction (see eq 7) despite the fact that dendrimers are physically different than the linear polymers for which the theory was originally derived.

Also given in the figure is the viscosity at $T_g$. A local minimum is shown for the viscosity similar to Fox and Flory's data for linear polystyrene at $T_g$.[26,27] The viscosity data essentially fall on a master curve as do the data at $T_o$ and the reference fractional free volume of 0.06. We cannot hypothesize why this local minimum occurs at $T_g$ for dendrimers (or linear polymers) at this point; however, the fact that both types of polymers exhibit similar behavior is interesting. It may be, also, that extrapolation of the data to $T_g$ creates this effect (i.e., it is an anomaly of the extrapolation).

We demonstrated in Figure 1 that the intrinsic viscosity has a maximum at a molecular mass of 4000 Da. Inspection of Figure 4 shows this is where the viscosity at $T_o$ approaches the linear master curve generated by determining the viscosity at a fractional free volume of 0.06. One can also notice the value of $f_o$ approaches a constant value at this molecular mass and above (see Table 2). Similarly, the viscosity at $T_g$ shows a minimum at (approximately) this molecular mass. (We reiterate that extrapolation of the viscosity, via the WLF theory, is fraught with error and the values at $T_g$ may be suspect.) This may indicate molecular reorganization within individual molecules (as discussed in the *Introduction*) is responsible for these effects. This hypothesis is based on our demonstrating $f_0$ is linear with $1/M$, indicating that the free volume theory is not applicable to dendrimers as just discussed.

Finally, eq 7 shows the viscosity should be linear with the molecular mass. Deviations from this proportionality are usually attributed to the density and monomeric friction coefficient being mass dependent. We have shown on a log–log graph there is curvature of the viscosity with molecular mass; however, above a certain molecular mass, the viscosity approaches a direct proportionality with molecular mass. In Figure 5 we have replotted the mono- and tridendron viscosity data on linear coordinates. The data for other temperatures were shifted according to eq 8 with $C_1$ and $C_2$ values of 7.21 ± 0.07 and 83 ± 1, respectively, determined from the higher molecular masses (> 4000 Da) in Table 2. This choice of WLF parameters shifts the data at higher molecular masses to a master curve.

The solid line represents the linear regression given by

$$\eta_0 \text{ (Pa s)} = (0.437 \pm 0.040)M \text{ (Da)} - (900 \pm 505)$$

which allows a monomeric friction coefficient of 7.0 × $10^{-7}$ N-s/m to be calculated from eq 7 [$\rho = 1000$ kg/m$^3$, $m_o = 121$ Da, which is the molecular mass of the branch unit, $L_m = 0.74$ nm (the value used for polystyrene[22]) were assumed]. When $\zeta_o$ is calculated like this it represents the limiting value at large molecular masses. This value for $\zeta_o$ is not too different from those for polystyrene.[22]

The data of Fox and Flory for polystyrene[26,27] at 413 K are compared with the viscosity of the dendrimer. The limiting fractional free volume at infinite molecular mass is almost equal to that for the dendrimers at this temperature ($f_\infty = 0.061$). One can clearly see the viscosity data for the linear polymer is quite curved compared with that of the dendrimer. The viscosity is lower for polystyrene at small molecular masses, yet, increases quite rapidly at higher molecular mass until it is greater than the viscosity of the dendrimer. Although the maximum molecular mass in the figure is below the critical molecular mass for polystyrene, where the viscosity increases as $M^{3.4}$, the intermolecular interactions are such that the viscosity increases at a much faster rate despite the fractional free volume being approximately equal for the two types of polymers in this molecular mass region. We believe the inter- and intramolecular interactions for dendrimers are responsible for this behavior. Future studies may help clarify this unique issue.

**End-Substituted Monodendron and Hypercores.** The first matter considered is the interesting observation that the fractional free volume at the glass transition temperature, $f_g$, is equivalent for all dendrimers considered in this work. The average for the mono- and tridendrons is 0.032 ± 0.002 (see Table 2). The end-substituted monodendron and hypercores have values of 0.030 and 0.032, respectively. Fox and Flory's supposition[26] that the glass transition represents an iso-free volume state appears true for all the dendrimers studied here.

The fractional free volume at the reference temperature, $f_o$, for the end-substituted monodendron is quite small, as seen in Table 2 (0.049 compared with ~0.06). This result certainly contributes to the extremely high value of the viscosity (Figure 4). Yet, when corrected to the reference fractional free volume of 0.06, the viscosity is still greater than the viscosity of the virgin mono- or tridendron by at least an order of magnitude. The same result is true when the viscosity is calculated at $f_g$. This result certainly indicates the end groups have a substantial effect on the viscosity even under iso-free volume conditions. The effect is lesser on $T_g$, although substantial (see Table 1).

Similar effects are noted for the hypercores, although deviations for the WLF parameters and viscosity are less. The viscosity, corrected to a constant fractional free volume of 0.06, is larger than the viscosity of the mono- and tridendrons (see Figure 4). A power law slope of 1.18 is obtained, which is slightly greater than the slope for mono- and tridendrons. Considering the physical structure of the hypercores is different from the "normal" dendrimers, the fact that the viscosity is only slightly higher for these molecules is appealing. It is difficult to make substantive conclusions for the viscosity of hypercores at $T_g$ because of scatter. Overall, the effect of end groups appears greater than the focal point of the molecule.

The thermal expansion coefficient for the free volume, $\alpha_f$, is greatest for the end-substituted monodendron. Clearly, the end groups substantially affect this quantity too. The overall effect is that the viscosity for the end-substituted monodendron is much more temperature dependent than the virgin monodendron of the same generation. This result may indicate a larger degree of molecular reorientation or nanophase separation for the end-substituted monodendron with temperature change. The viscosity of the hypercores is also slightly more temperature dependent than virgin dendrimers. Again, the temperature dependence is lesser than end-substituted monodendrons, indicating end groups are more important than the core.

## Conclusion

It was found that the intrinsic viscosity, $\Delta T_g$ [glass transition temperature ($T_g$) at infinite molecular mass less $T_g$ for a given molecular mass] and fractional free volume and viscosity ($\eta_0$) at the reference temperature all scale with molecular mass ($M$) for mono- and tridendrons. It may be concluded that $M$ rather than generation number or number of ends per $M$ is the correct scaling parameter.

Also, $\Delta T_g$ data for several end-substituted monodendrons fall on the same master curve as that for virgin monodendrons when plotted versus $M$. This result suggests a unique form for the $M$ dependence of $T_g$, where $T_g$ at infinite $M$ is dependent on the end groups and $\Delta T_g$ is not. This suggestion is contrary to free volume theory that has been used to relate the number and type of end groups to $\Delta T_g$.

Despite this apparent limitation in the utility of free volume theory to dendrimers, it is possible to correct the terminal viscosity to constant fractional free volume, and an (almost) linear relation between $\eta_0$ and $M$ is obtained in agreement with the Rouse model. The viscosity for hypercores continues this scaling for mono- and tridendrons, although the values are slightly higher. The end-group-substituted monodendron shows a viscosity that is much greater than the master curve even when corrected to the reference fractional free volume. It is concluded that end groups influence the viscosity to a much greater extent than the core.

## Appendix

Here the derivation of eq 3 is given. Stutz and coworkers[15,16] start with DiBennedetto's equation[31] for the glass transition of cross-linking systems which can be written as

$$\frac{T_g}{T_g^p} = 1 + k_2 \frac{X}{1 - X}$$

where $T_g^p$ is the glass transition temperature of the backbone at conversion $p$ and $X$ is the cross-link density which is given by

$$X = \frac{\text{number of units as branches}}{\text{total number of units}} = \frac{N_b^{g-1} - 1}{N_b^g - 1}$$

The conversion is assumed by Stutz et al.[15] to affect $T_g^p$ by

$$T_g^p = T_g^\infty - k_1[1 - p]$$

where $T_g^\infty$ is the backbone glass transition temperature at infinite conversion. The quantity $[1 - p]$ is the ratio of the number of ends in a molecule after reaction ($N_E$) to the number of ends prior to reaction ($N_{E0}$). $N_E$ is $N_c N_b^g + C$, whereas $N_{E0}$ is $N_c[N_b + 1][N_b^g - 1]/[N_b - 1]$, which yields

$$1 - p = \frac{\text{number of ends in a molecule}}{\text{total number of ends prior to reaction}} = \frac{[N_c N_b^g + C]\,[N_b - 1]}{N_c[N_b + 1][N_b^g - 1]}$$

The constant $C$ takes into account the extra end (i.e., the core) that is present in the monodendron. Didendrons and higher dendrimers do not have this extra “dangling” end because the core is attached to multiple dendrimers. Therefore, $C$ is one for monodendrons and zero for multiple dendrimers attached to a core.

The glass transition temperature at infinite generation number is equal to

$$T_{g\infty} = \left[T_g^\infty - k_1\frac{N_b - 1}{N_b + 1}\right]\left[1 + k_2\frac{1}{N_b - 1}\right]$$

Combining the equations just presented to yield $\Delta T_g$ and performing some algebraic manipulation yields eq 3.

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## References and Notes

(1) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 138.
(2) de Gennes, P. G.; Hervert, H. *J. Phys. (Paris)* **1983**, *44*, 351.
(3) Naylor, A. M.; Goddard, W. A., III; Kiefer, G.; Tomalia, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2339.
(4) Lescanec, R. L.; Muthukumar, M. *Macromolecules* **1990**, *23*, 2280.
(5) Mansfield, M. L.; Klushin, L. I. *Macromolecules* **1993**, *26*, 4262.
(6) Mansfield, M. L. *Polymer* **1994**, *35*, 1827.
(7) Murat, M.; Grest, G. S. *Macromolecules* **1996**, *29*, 1278.
(8) Aharoni, S. M.; S. M.; Crosby, C. R., III; Walsh, E. K. *Macromolecules* **1982**, *15*, 1093.
(9) Mourey, T. H.; Turner, S. R.; Rubinstein, M.; Hawker, C. J.; Fréchet, J. M. J.; Wooley, K. L. *Macromolecules* **1992**, *25*, 2401.
(10) Tomalia, D. A.; Hedstrand, D. M.; Wilson, L. R. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1990.
(11) de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 138.
(12) Fréchet, J. M. J. *Science* **1994**, *263*, 1710.
(13) Wooley, K. L.; Hawker, C. J.; Pochan J. M.; Fréchet, J. M. J. *Macromolecules* **1993**, *26*, 1514.
(14) Kim, Y. H.; Beckerbauer, R. *Macromolecules* **1994**, *27*, 1968.
(15) Stutz, H.; Illers, K.-H.; Mertes, J. *J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 1483.
(16) Stutz, H. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 333.
(17) Gibbs, J. H.; DiMarzio, E. A. *J. Chem. Phys.* **1958**, *28*, 373.
(18) Pietralla, M.; Mayr, P.; Weishaupt, K. *J. Non-Cryst. Solids* **1996**, *195*, 199.
(19) Heuer, A.; Speiss, H. W. *J. Non-Cryst. Solids* **1994**, *176*, 294.
(20) Hawker, C. J.; Farrington, P. J.; Mackay, M. E.; Wooley, K. L.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1995**, *117*, 4409.
(21) Farrington, P. J. *Polymer Structure, Dynamics and Viscoelasticity*; Ph.D. Thesis, The University of Queensland, Queensland, Australia, 1995.
(22) Ferry, J. D. *Viscoelastic Properties of Polymers, Third Edition*; John Wiley and Sons: Sydney, 1980.
(23) Allen, V. R.; Fox, T. G. *J. Chem. Phys.* **1964**, *41*, 337.
(24) Berry, G. C.; Fox, T. G. *Adv. Polym. Sci.* **1968**, *5*, 261.
(25) Williams, M. L.; Landel, R. F.; Ferry, J. D. *J. Am. Chem. Soc.* **1955**, *77*, 3701.
(26) Fox Jr., T. G.; Flory, P. J. *J. Appl. Phys.* **1950**, *21*, 581.
(27) Fox Jr., T. G.; Flory, P. J. *J. Polym. Sci.* **1954**, *14*, 315.
(28) Colby, R. H.; Fetters, L. J.; Graessley, W. W. *Macromolecules* **1987**, *20*, 2226.
(29) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.
(30) Wooley, K. L.; Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4252.
(31) DiBennedetto, A. T. *J. Polym. Sci. Part B: Polym. Phys* **1987**, *25*, 1949.

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