# Effects of Molecular Variables and Architecture on the Rheological Behavior of Dendritic Polymers

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ABSTRACT: Comparisons of simple shear, oscillatory, and creep flow rheological behaviors are presented for several poly(propylenimine) dendrimers (DAB), hyperbranched (HBP) polyesters, and poly(ether−imide) (PEI) HBPs. Variables examined include molecular weight, degree of branching, nature of peripheral groups, and molecular architecture. In simple shear, DAB dendrimers and HBP polyesters exhibited a Newtonian behavior, and both showed a similar relationship between zero shear rate viscosity, $\eta_0$, and molecular weight, $M_w$. In oscillatory experiments, amine end-capped DAB dendrimers and HBP polyesters exhibited Newtonian behavior, while the nitrile end-capped DAB dendrimers showed a Rouse-like frequency dependence of both moduli. A fit of Fox and Flory theory to the fractional free volume data obtained by WLF analysis of DAB dendrimers suggests that the volume free fraction of end groups is independent of generation number. The data on PEI HBPs suggest that at the lowest molecular weight ($M_n \sim 4300$) the rheological behavior is Newtonian; however, the higher molecular weight solutions showed shear thinning and normal stress effects, both of which increased with the decrease in the degree of branching (DB). From the concentration dependence of storage and loss moduli, it is observed that intermolecular interactions of PEI HBPs are dominated by hydrodynamics at low concentrations (≤30 wt %), by coil overlap at intermediate concentrations (~35 wt %), and by entanglements at higher concentrations (≥40 wt %).

## Introduction

Polymers have traditionally been classified according to their chain architecture into three categories: linear, cross-linked, and branched molecules. Recent developments in the synthesis of highly branched systems have led to a more general classification scheme that mimics the dendritic branching of trees, appropriately called dendritic macromolecules.[1] The synthesis of dendritic polymers was first introduced by Vogtle[2] in 1978 and developed in the mid-1980s by Tomalia,[3] Newkome,[4] Frechet,[5] and others (see Frechet[6] for a review). The family of dendritic macromolecules is further divided into two subgroups: dendrimers and hyperbranched polymers (HBP). Both consist of highly branched structures emanating from a central core or focal points with multiple end groups. However, only perfect dendrimers have precise functionality and end group multiplicity. Synthesis of perfect dendrimers involves stepwise iterative addition of generations with numerous intermediate purification steps.[6] Hyperbranched polymers, on the other hand, can be synthesized by "one-pot" reactions of $AB_x$-type monomers, where $x \geq 2$.[6,7] While the structure of hyperbranched polymers obtained by this method is highly branched, such branching does not imply a dendrimer topology.[8] Consequently, hyperbranched polymers exhibit properties that are intermediate between perfect dendrimers and linear polymers.

Because of the close relationship between rheology and processing properties, characterization of the rheological flow behavior of dendritic polymers is important. Such studies can provide insights into the intermolecular interactions and the effects that molecular variables such as generation number, nature of peripheral functional groups, and degree of branching have on bulk properties. Despite this importance, relatively few studies, particularly studies showing comparisons of the rheological behavior of dendrimeric and hyperbranched systems, have been reported. While some advances have been made in the study of bulk properties of perfect dendrimers,[9−11] work with hyperbranched polymers is lagging. Therefore, the goal of the present study is to investigate the effects that molecular variables such as degree of branching, molecular weight, nature of peripheral groups, and molecular architecture have on the bulk properties of dendritic materials. In this paper we present and compare the rheological behavior of poly(propylenimine) dendrimers, aliphatic hyperbranched polyesters, and poly(ether−imide) hyperbranched polymers.

## Experimental Section

**Materials.** Materials analyzed in this study include perfect dendrimers produced by a divergent polymerization process and hyperbranched polymers synthesized by a "one pot" $AB_2$ polymerization and a traditional one-step approach using a core molecule. Poly(propylenimine) dendrimers based on the diaminobutane (DAB) core molecule were obtained from DSM (The Netherlands). Their synthesis involves the repetitive reaction sequence involving a Michael addition of 2 equiv of acrylonitrile to a primary amine group, followed by a hydrogenation of the nitrile groups to primary amine groups.[12] Dendrimers with 4, 8, 16, 32, and 64 amine end groups and 16, 32, and 64 nitrile groups were studied. Additional properties of the DAB dendrimers are listed in Table 1.

Two types of hyperbranched polymers were studied. The first, supplied by Perstorp (Sweden), are aliphatic hyperbranched (HBP) polyesters with hydroxyl groups at the surface.[13] The synthesis of these polymers involves a reaction of core molecules and chain extenders in stoichiometric ratio.[13] The polymers produced by this approach are polydisperse and resemble dendrimers in that they consist of a core, from which branches extend, giving a core/shell structure. The degree of branching is reported to be 43%.[14] The second group consisted of poly(ether−imide) (PEI) hyperbranched polymers prepared in our laboratories using "one pot" $AB_2$ polymerization.[15] The

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**Table 1. Material Properties of Poly(propylenimine) Dendrimers**

| generation | theor mol wt | name | theor end groups | $T_g$ (°C) |
|---|---|---|---|---|
| 2.5 | 1622 | DAB(CN)$_{16}$ | 16 CN | −47 |
| 3.5 | 3385 | DAB(CN)$_{32}$ | 32 CN | −45 |
| 4.5 | 6910 | DAB(CN)$_{64}$ | 64 CN | −40 |
| 1 | 317 | DAB(NH$_2$)$_4$ | 4 NH$_2$ | −107 |
| 2 | 773 | DAB(NH$_2$)$_8$ | 8 NH$_2$ | −97 |
| 3 | 1687 | DAB(NH$_2$)$_{16}$ | 16 NH$_2$ | −90 |
| 4 | 3514 | DAB(NH$_2$)$_{32}$ | 32 NH$_2$ | −87 |
| 5 | 7166 | DAB(NH$_2$)$_{64}$ | 64 NH$_2$ | −84 |

**Table 2. Material Properties of Perstorp Polyester Hyperbranched Polymers**

| generation | $M_w$ (g/mol) (SEC) | $M_w/M_n$ | name | theor end groups |
|---|---|---|---|---|
| 2 | 2100 | 1.3 | Perstorp 1 | 16 OH |
| 3 | 3500 | 1.5 | Perstorp 2 | 32 OH |
| 4 | 5100 | 1.8 | Perstorp 3 | 64 OH |
| 5 | 7500 | 2.5 | Perstorp 4 | 128 OH |

**Table 3. Material Properties of the Poly(ether−imide) Hyperbranched Polymers**

| name | $M_w$ (GPC) | $M_n$ | $T_g$(°C) | DB |
|---|---|---|---|---|
| PEI 1 | 7 600 | 4 300 | 180 | 0.68 |
| PEI 2.5 | 47 000 | 19 000 | 180 | 0.64 |
| PEI 5 | 47 000 | 17 000 | 180 | 0.59 |
| PEI 10 | 90 000 | 24 000 | 180 | 0.44 |
| PEI 20 | 77 000 | 18 000 | 180 | 0.42 |

degree of branching of the samples, determined by NMR, ranged from 42% to 68%. Properties of the HBP polyesters and the PEI HBPs are listed in Tables 2 and 3, respectively. The data presented in Table 3 are for PEI HBPs extracted at different reaction times and were found to correlate with the degree of branching as shown.

**Experiment.** GPC data for the poly(ether−imide) HBPs were obtained in THF at 35 °C. Gel permeation chromatography (GPC) measurements were performed with a Waters 510 HPLC pump, Waters 996 photodiode array detector, and a series of three Waters styragel HR 4E 7.8 × 300 mm columns, which were calibrated with narrow molecular weight polystyrene standards.

Simple shear, oscillatory, and creep measurements were made on a TA Instruments, AR 1000-N, constant stress rheometer using a cone and plate geometry. Oscillatory experiments were performed in the linear viscoelastic (LVE) region in the frequency range 0.1−50 Hz, and simple shear experiments were completed over several decades of shear rates. Temperature control was achieved with a Peltier plate (0−100 °C) and extended temperature modules (100−400 °C) to a precision of 0.1 °C. In addition to viscosity, the normal stress response in simple shear flow was also measured. A nitrogen atmosphere was used with the hyperbranched polyesters to prevent oxidation.

Because of their high glass transition temperature, melt viscosity measurements of the poly(ether−imide) HBP were not possible. Instead, concentrated solutions ranging from 20 to 45 wt % in 1,2-dichlorobenzene were used. A solvent trap was used to prevent evaporation, and experiments were performed in the temperature range from 5 to 25 °C.

## Results and Discussion

**Poly(propylenimine) Dendrimers (DAB) and Hyperbranched Polyesters.** Figures 1 and 2 show viscosity results for the DAB dendrimers (generations 1−5) and the polyester HBPs (generations 2−5), respectively. For all molecular weights, the viscosity was found to be independent of shear rate, characteristic of a Newtonian fluid. Since the viscosity shows no shear rate dependence, we refer to it as the zero shear rate viscosity, $\eta_0$. Newtonian behavior was further evident in creep experiments, constant shear rate being reached almost instantaneously with negligible recovery. While this response was anticipated for the DAB dendrimers and has previously been observed with PAMAM[11] and poly(benzyl ether)[10] dendrimers, it is interesting that the polyester HBPs, despite their lower degree of branching and more open structure, do not exhibit viscoelastic behavior.

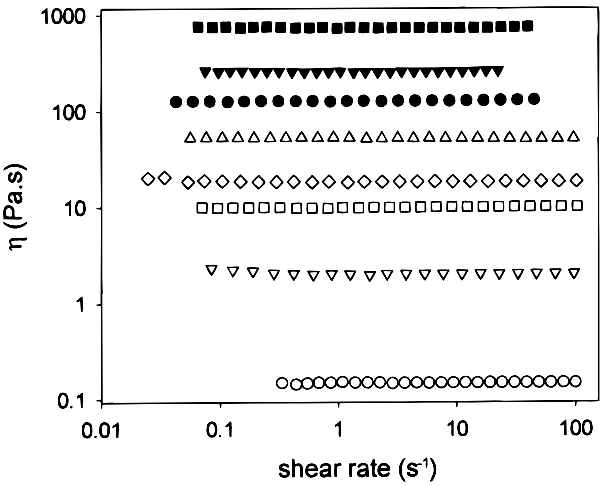

**Figure 1.** Viscosity behavior of DAB dendrimers with nitrile (CN) and amine (AM) end groups in simple shear flow at 20 °C: ●, DAB(CN)$_{16}$; ▼, DAB(CN)$_{32}$; ■, DAB(CN)$_{64}$; ○, DAB-(AM)$_4$; ▽, DAB(AM)$_8$; □, DAB(AM)$_{16}$; ◇, DAB(AM)$_{32}$; △, DAB-(AM)$_{64}$.

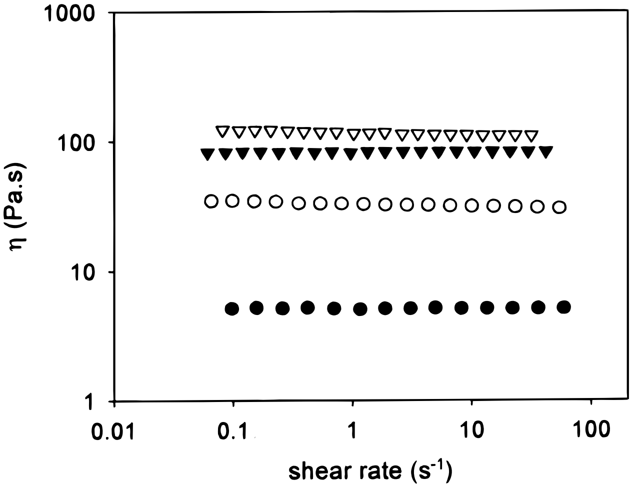

**Figure 2.** Viscosity behavior of the Perstorp hyperbranched polyesters in simple shear flow at 100 °C: ●, Perstorp 2; ○, Perstorp3; ▼, Perstorp 4; ▽, Perstorp 5.

Figure 3 shows the relationship between zero shear-rate viscosity and molecular weight for the polyester HBPs and DAB dendrimers. The zero shear-rate viscosity, $\eta_0$, for both systems exhibits a gradual decrease in slope with increasing molecular weight. For the dendrimer system, such behavior is believed to reflect a transition from more open, spherical structures at lower generations, to closed globular structures at higher generations. Our data suggest a similar phenomenon occurs with the polyester HBPs. For most linear polymers the relationship between viscosity and molecular weight exhibits a general trend where two distinct viscosity dependencies exist: $\eta_0 \sim M_w$ at lower molecular weights and $\eta_0 \sim M_w^{3.4}$ at higher molecular

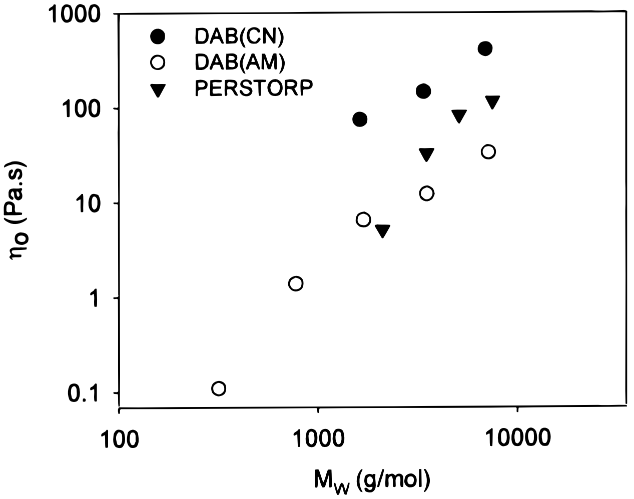

**Figure 3.** Molecular weight dependence of viscosity for Perstorp hyperbranched polyesters at 100 °C and DAB dendrimers at 25 °C.

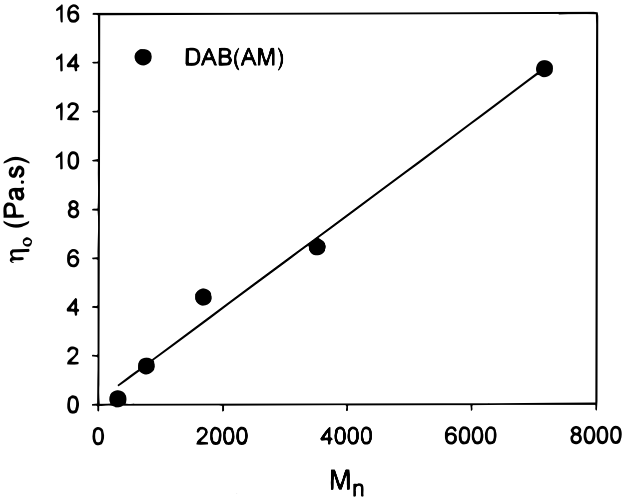

**Figure 4.** Plot of viscosity as a function of $M_w$ for DAB(AM) dendrimers at extrapolated temperatures of $T_g$ + 120 °C.

weights. The molecular weight at which the transition occurs, the so-called critical molecular weight, is associated with the onset of entanglements. Since a sharp break in the plot of log $\eta_0$ vs log $M_w$ is not observed and the behavior in simple shear is Newtonian, it can be inferred that intermolecular interactions of the polyester HBPs are similar to those of perfect dendrimers and are, therefore, free of entanglements.

**Temperature Effects.** As shown above, DAB dendrimers and polyester HBPs show a unique relationship between $\eta_0$ and $M_w$. However, since the glass transition temperature of these polymers varies with molecular weight, it is necessary to account for the effects of $T_g$ on $\eta_0$. To do this, the viscosity data were fit to the Arrhenius equation. The resultant viscosity of the amine end-capped DAB dendrimers, evaluated at $T_g$ + 120 °C, is shown as a function of $M_w$ in Figure 4. From this plot, we conclude that the molecular weight dependence is similar to that of linear polymers below $M_c$ and in accordance with the Rouse model prediction, $\eta_0 = KM$.

As seen in Figure 5, the Arrhenius activation energy of the DAB dendrimers increases at low generations and reaches a steady value at generation 3 ($M_n \sim 1687$ g/mol). Uppuluri et al.[11] observed a similar behavior with PAMAM dendrimers, which they associate with the reduction of intermolecular hydrogen bonding caused by the onset of "closure" of the outer dendrimer surface. As shown in Figure 5, the polyester HBPs exhibit a similar molecular weight dependence of the activation energy.

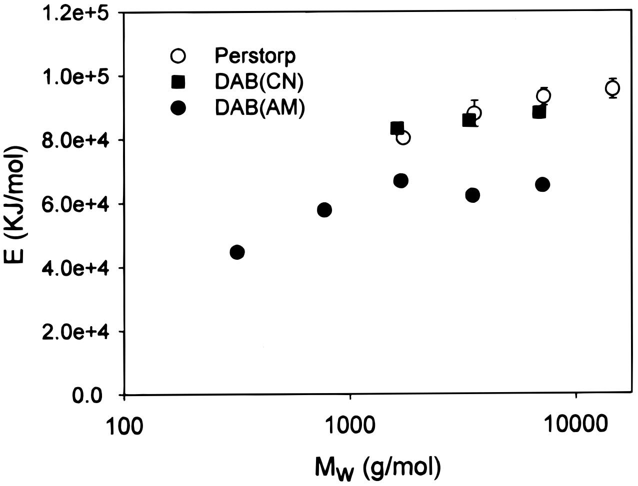

**Figure 5.** Arrhenius activation energy vs molecular weight for DAB dendrimers and Perstorp polyester HBPs. With the exception of the Perstrop system, error bars are smaller than symbols.

The temperature dependence of the zero-shear rate viscosity was also analyzed using the WLF equation,[16]

$$\log \frac{\eta(T)}{\eta(T_0)} = \log a_T = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)} \tag{1}$$

The underlying assumptions of the WLF equation are that the fractional free volume, $f$, increases linearly with temperature and that the mobility at any temperature depends primarily on the free volume.[17] Incorporating these concepts, the following relations between the constants, $C_1$ and $C_2$ , and the fractional free volume are obtained,

$$C_1 = B/(2.303f) \quad \text{and} \quad C_2 = f/\alpha_f \tag{2}$$

where $f$ is the fractional free volume at the reference temperature, and $\alpha_f$ is the thermal expansion coefficient. As shown in Figure 6, the data for the amine end-capped DAB dendrimers exhibit a good fit. Similar good fits were obtained for the nitrile end-capped DAB dendrimers and the polyester HBPs. The resultant parameters for the DAB dendrimers are given in Table 4.

Since $C_1$ is inversely proportional to $f$, the data in Table 4 show that the fractional free volume decreases with molecular weight for the DAB dendrimers. Farrington et al.[10] found similar trends with poly(benzyl ether) dendrimers; however, they argued that since fractional free volume depends on the number of end groups, comparison of dendrimers of different generations using WLF theory is inappropriate. According to the theory of Fox and Flory, the free volume of a polymer molecule should be proportional to $1/M_n$.[17] Thus, with the addition of free volume due to imperfect packing of end groups, one has

$$f = f_0 + A/M_n \tag{3}$$

where $A$ is related to the end groups, and $f_0$ is the limiting fractional volume at infinite molecular weight.

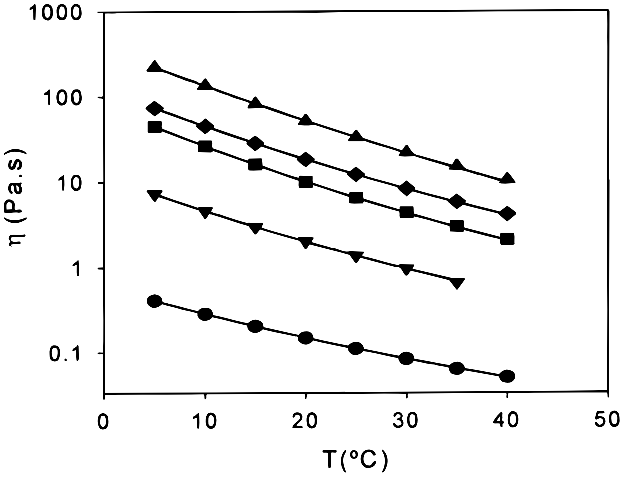

**Figure 6.** WLF equation fit of amine end-capped DAB dendrimers at the reference temperature of 25 °C: ●, DAB-(AM)$_4$; ▼, DAB(AM)$_8$; ■, DAB(AM)$_{16}$; ◆, DAB(AM)$_{32}$; ▲, DAB-(AM)$_{64}$.

**Table 4. WLF Parameters for Poly(propylenimine) Dendrimers at $T_{ref}$ of 25 °C**

| name | MW | no. of ends | C1 | C2 |
|---|---|---|---|---|
| DAB(CN)16 | 1622 | 16 | 21.03 | 195.8 |
| DAB(CN)32 | 3385 | 32 | 25.48 | 226.2 |
| DAB(CN)64 | 6910 | 64 | 26.52 | 228.8 |
| DAB(AM)4 | 317 | 4 | 9.19 | 160.2 |
| DAB(AM)8 | 773 | 8 | 12.08 | 165.1 |
| DAB(AM)16 | 1687 | 16 | 13.72 | 162.5 |
| DAB(AM)32 | 3514 | 32 | 14.20 | 177.9 |
| DAB(AM)64 | 7166 | 64 | 20.39 | 234.8 |

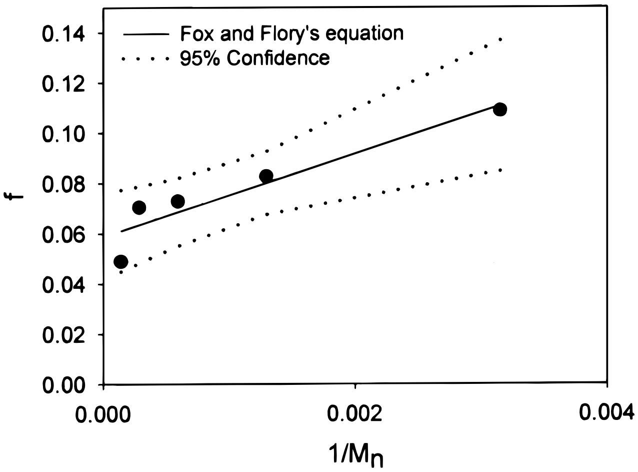

**Figure 7.** Fractional free volume from WLF equation for DAB(AM) dendrimers at the reference temperature of 25 °C plotted verses $1/M_n$. The 95% confidence limits also shown.

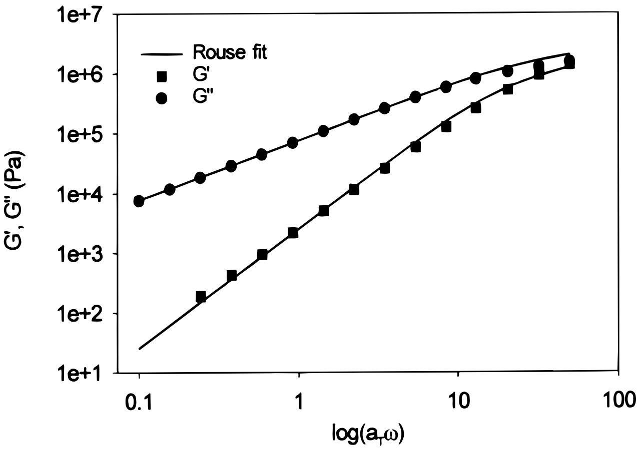

**Figure 8.** Rouse fit of DAB(CN)$_{64}$ oscillatory data at the temperature of 0 °C.

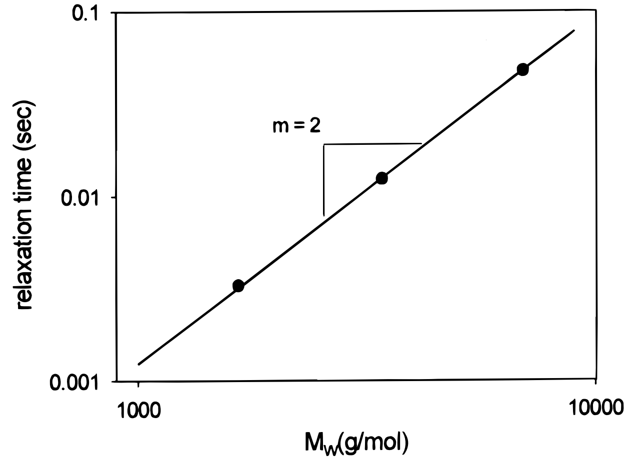

**Figure 9.** Longest relaxation time calculated from Rouse model fit to oscillatory data of DAB(CN) at the temperature of 0 °C.

This correlation works well for linear polymers, and it has been shown that the additional free volume associated with each end group is about 30% of the total volume associated with each monomer.[17] Since for dendrimers the number of end groups increases with each generation, eq 3 can be modified to account for additional free volume as follows,

$$f = f_0 + A(N_E/M_n) \quad (4)$$

where $N_E$ is the number of end groups.[10] The best fit of eq 4 to the fractional free volume of the amine end-capped DAB dendrimers yielded values for $A$ and $f_0$ of 13.4 and −0.0589, respectively. Since negative values of $f_0$ are unphysical, eq 4 does not apply. On the other hand, Figure 7 shows that $f$ exhibits a linear relationship with $1/M_n$ consistent with the Fox and Flory equation. The values of $f_0$ and $A$ obtained from the plot are 0.059 and 16.5, g/mol, respectively. The value for $f_0$ is identical to that obtained for poly(benzyl ether) dendrimers.[10] The constant value of $A$ from our data suggests that additional free volume due to end groups remains constant, which could be accomplished by back-folding of the end groups into the void space in the interior of the molecule. Since the number of end groups increases with each generation, the back-folding effect is expected to increase in order to keep the fractional free volume of the end groups constant. An increase in back-folding would suggest the void space within the molecule decreases, forming a more compact (space-filling) structure. Such behavior is in qualitative agreement with the molecular dynamics study of Scherrenberg et al.[18] for amine end-capped DAB dendrimers, which indicates that end groups are dispersed throughout the molecule. The density distribution exhibits a plateau region and a monotonic decrease toward the exterior of the molecule.[18] In agreement with our result, this uniform density profile, especially seen at higher generations, indicates a space-filling structure. Our WLF analysis of the polyester HBP indicates that their fractional free volume did not change considerably with molecular weight.

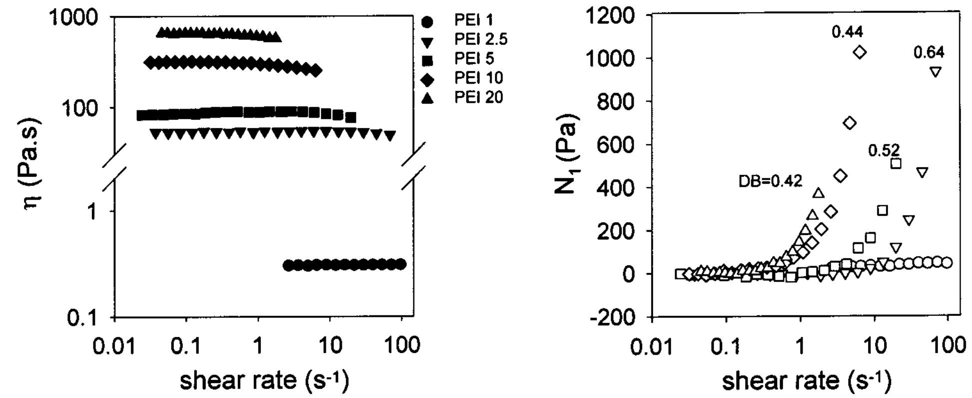

**Figure 10.** Simple shear flow viscosity and $N_1$ as a function of shear rate of 40 wt % solution of PEI HBPs in 1,2-dichlorobenzene at 25 °C.

The results of dynamic experiments further indicate that entanglement couplings do not dominate the intermolecular interaction of the polyester HBP and DAB dendrimers. In the frequency and temperature range of our experiments, the behavior of polyester HBP and amine end-capped dendrimers was found out to be essentially Newtonian, $G' \sim 0$ and $G'' \sim \omega$. This behavior is in agreement with our results from simple shear and creep experiments where we observed constant viscosity and negligible recovery.

On the other hand, the data shown in Figure 8 for nitrile end-capped DAB dendrimers exhibit a frequency dependence of the storage and relaxation moduli consistent with Rouse behavior. As seen, the Rouse model predictions of storage and relaxation modulus fit the data well in the terminal regime; however, there is some deviation at higher frequencies. Furthermore, Figure 9 shows that the longest relaxation times obtained from the Rouse model, $\lambda_1$, are proportional to $M^2$, consistent with the Roussian behavior. For polymers above the entanglement critical length, the longest relaxation time is proportional to $M^{3.4}$. Consequently, since these polymers obey the Rouse model, we can infer that entanglement coupling of the chains does not occur.

**Poly(ether−imide)s.** Poly(ether−imide) (PEI) HBPs are completely amorphous; however, at temperatures as high as 350 °C they did not flow. Therefore, to examine the rheological behavior of these polymers, we prepared concentrated solutions in 1,2-dichlorobenzene, ranging from 20 to 45 wt %. From this study, we were able to explore the difference in intermolecular interactions of these polymers as a function of concentration and thereby compare their behavior with that of linear polymers and perfect dendrimers.

The viscosity and first normal stress difference ($N_1$) behaviors in simple shear flow of the 40 wt % solution of PEI hyperbranched polymers in 1,2-dichlorobenzene are presented in Figure 10. The range of response, from Newtonian at the lowest molecular weight to shear thinning at higher molecular weights, is observed; however, the magnitude of the shear viscosity, the onset of shear thinning, and rise of normal stress effects correlate with the degree of branching (DB). The Newtonian behavior of the lowest molecular weight sample ($M_n \sim 4300$ g/mol) is not surprising since the polyester HBPs of comparable molecular weight showed a similar behavior. Figure 11 shows a replot of $N_1$ data on log−log coordinates from which the power law dependence with shear rate becomes apparent. As seen, in the lower shear rate range, $N_1$ scales as (shear rate)$^2$ (i.e., constant first normal stress coefficient) and tapers off to a (shear rate)$^{1.5}$ (i.e., shear-thinning) dependence at higher shear rates. The dependence of $N_1$ is similar to that seen for other viscoelastic fluids and has been associated with entanglement coupling in linear polymers.[17] These results suggest that the PEI HBPs with lower DB are capable of a higher degree of coil overlap and entanglement coupling.

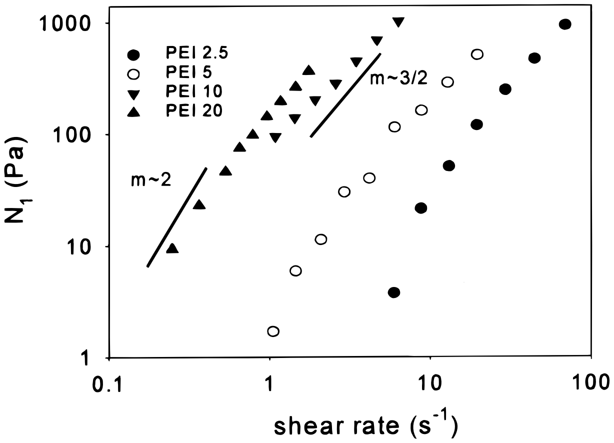

**Figure 11.** Plot of $N_1$ vs shear rate on logarithmic scale of 40 wt % solutions of PEI HBP in 1,2-dichlorobenzene at 25 °C.

A similar change in intermolecular interactions can also be observed with concentration dependence, an example of which is shown in Figure 12. In the concentration range up to 30 wt %, the viscosity is independent of shear rate and $N_1$ is negligible. However, at concentrations above 30 wt %, the viscosity and $N_1$ both exhibit a shear rate dependence that clearly increases with concentration, suggesting a higher degree of entanglement.

Further evidence of entanglement interactions is exhibited by the concentration dependence of the storage and relaxation moduli shown in Figure 13. At 30 wt %, the behavior follows the Zimm model, i.e., $G''/G' = 3^{1/2}$, and both moduli are proportional to $\omega^{2/3}$ in the intermediate frequency range. The underlying assumptions of this model are that concentration is low enough that coil overlap does not occur and hydrodynamic interactions dominate the behavior. With increasing concentration, Zimm behavior yields to the Rouse regime in which hydrodynamic forces are assumed to be screened by coil overlap.[19] According to our data, this occurs at a concentration of 35 wt %. At concentrations of 40 wt % and above, the coils are highly overlapping, and at

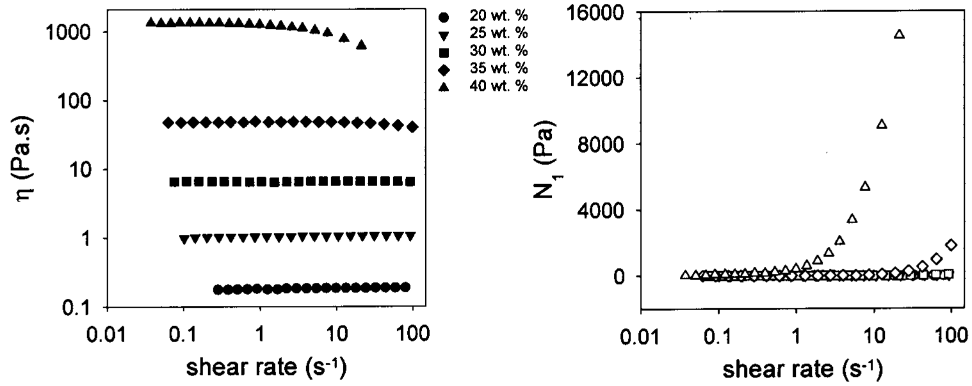

**Figure 12.** Simple shear flow viscosity and normal force as a function of shear rate for concentrated solutions of PEI 2.5 HBP in 1,2-dichlorobenzene at 5 °C.

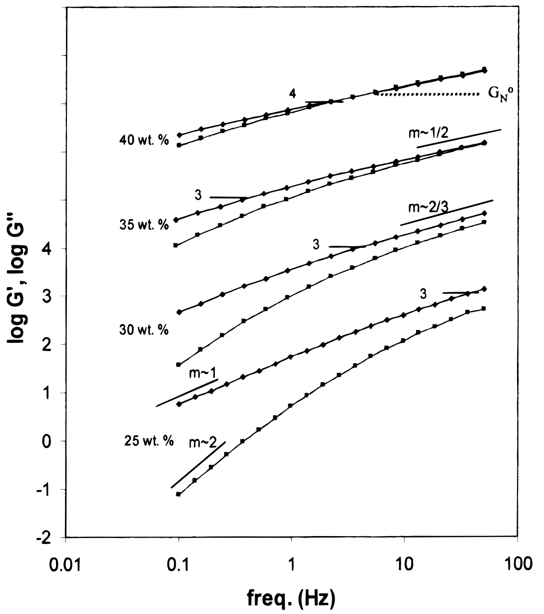

**Figure 13.** *G*′ and *G*″ versus frequency for PEI HBPs at concentrations indicated. Ordinates are shifted vertically.

intermediate frequencies *G*″ crosses *G*′. The appearance of a plateau modulus, $G_N{}^o$, indicates the beginning of a new regime where *G*′ is insensitive to frequency.[18]

## Conclusions

The results of our study show the rheological behavior of dendritic polymers ranging from Newtonian to viscoelastic. As expected, this behavior is affected by molecular variables, such as DB and $M_w$; however, the molecular architecture appears to be the most important factor determining the nature of the intermolecular interactions and consequently the rheological behavior. Two types of dendritic architecture have been compared in this study. The first group, DAB dendrimers and polyester HBPs, are multilayered structures whose rheological behavior, in the molecular range studied, indicates no intermolecular entanglement formation. For both polymers, this behavior is further reflected in the relationship between $\eta_0$ and $M_w$. The similarity of the rheological behavior of polyester HBPs to perfect dendrimers suggests that divergently synthesized HBP, whose preparation involves less intermediate purification, may possess similar attractive properties previously only attributed to perfect dendrimers.

The PEI HBPs, on the other hand, are characterized by a more open structure that apparently promotes a significant degree of coil overlap and entanglement coupling. In consequence, the higher molecular weight ($M_n \sim 20\,000$) samples exhibited viscoelastic effects that correlate with the decrease in the degree of branching. From the concentration dependence of storage and loss moduli, it is observed that intermolecular interactions are dominated by hydrodynamics at low concentrations, by coil overlap at intermediate concentrations, and by entanglements at higher concentrations. This behavior suggests that the rheological properties of PEI HBPs are closer to those of linear polymers than perfect dendrimers.

Finally, the fractional free volume behavior of the DAB dendrimers indicates that end groups back-fold into the interior of the molecule. Our results indicate that back-folding increases with generation number, thereby creating more uniform density profiles in higher generation dendrimers, in agreement with molecular dynamics simulations.[18,20–24]

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