J. Am. Chem. Soc. **1995,** *117,* 4409−4410

Molecular Ball Bearings: The Unusual Melt Viscosity Behavior of Dendritic Macromolecules

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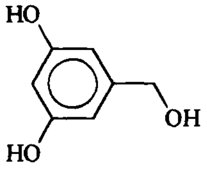
Received January 6, 1995

Dendritic macromolecules are a new class of highly branched macromolecules that have received a large amount of attention recently.[1] The uniqueness of these 3-dimensional polymers is related to the ability to control their size, shape, molecular weight, topology, and surface chemistry to an extent unprecedented in polymer science.[2,3] While a large variety of novel structures have been synthesized,[4] the thorough investigation of the physical properties of these materials has lagged. This is unfortunate, since a number of reports have appeared suggesting exciting and unusual behavior.[5] For example, a unique maximum in the relationship between intrinsic viscosity and molecular weight has been demonstrated,[6] a behavior that is consistent with the adoption of a globular structure as the molecular weight of the dendrimer increases. Although not yet experimentally proven, theoretical predictions[7] suggest that the surface of regular dendrimers should become increasingly congested as their molecular weight increases, eventually becoming dense packed. Meijer[8] has elegantly shown that small molecules can be trapped in a dendrimeric "box" which may be a demonstration of this surface congestion. This surface congestion, coupled with the high degree of branching, is expected to contribute greatly to the prevention of entanglements between dendrimer molecules. As a result, entanglement-dominated physical properties such as melt viscosity would be severely affected. In this report, we detail the effect of molecular weight, and hence surface congestion, on the melt viscosity behavior of dendritic macromolecules.

Dendritic polyether macromolecules[9] based on 3,5-dihydroxybenzyl alcohol, **1**, as the monomer unit were used in this study. These materials were prepared by the convergent growth approach where the synthesis begins at the chain ends, or terminal groups, and gives dendrons of various generations such as [G-4]-Br. Reaction of these dendrons with polyfunctional cores, such as 1,1,1-tris(4′-hydroxyphenyl)ethane, or the recently reported hypercores,[10] then leads to dendrimers such as [G-4]$_3$-[C].[11] Samples of these dendritic macromolecules, which are amorphous solids at room temperature, were compression molded into 7.9 mm disks at 50 °C under vacuum. Rheological measurements were then taken using a modified Rheometrics fluids spectrometer with 7.9 mm parallel plates and a plate separation of between 0.5 and 1.0 mm. No gap effect was observed. The sample temperature was controlled to within 1 °C of the set point, and the experiments were conducted under nitrogen to force convection. No oxidation or degradation of the samples was observed even after prolonged testing. Dynamic tests were performed in the linear viscoelastic region using strains between 1% and 50%. It was found that the complex viscosity was equal to the steady-shear viscosity, in accord with the Cox−Merz rule, and independent of the frequency in the range studied.



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Traditionally, the relationship between zero-shear viscosity and molecular weight of polymers is usually described by the power law

$$\eta_0 = KM^a$$

where the value of the exponent, a, is approximately 1.0 for low molecular weight polymers, but approaches a value of 3.4 as the molecular weight increases beyond a critical value, M_c. This transition around M_c is quite sharp and is believed to be associated with the onset of entanglement. While this relationship holds for all linear polymer systems, the unique nature of dendritic macromolecules, where entanglements are not expected to be a dominant process, may result in no observed change in a from the initial value of 1.0. Therefore no critical molecular weight, M_c, would be observed for dendrimers.

To investigate the melt viscosity behavior of dendrimers, the zero-shear viscosity at 80 °C for both polyether monodendrons, [G-3]-OH to [G-6]-OH, and tridendrons, [G-1]$_3$-[C] to [G-5]$_3$-[C], based on 1,1,1-tris(4′-hydroxyphenyl)ethane as a core unit was studied in detail. These dendrimers are essentially monodisperse with molecular weights in the range from 1256 to 20 993, and a logarithmic plot of melt viscosity versus molecular weight is shown in Figure 1. It is immediately apparent that the data for both the monodendrons and the tridendrons superimpose on a single curve, indicating that the viscosity of these molecules is dominated by their molecular weight, regardless of the nature of the focal point group or the generation

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(11) For an explanation of the nomenclature used for these dendrimers, see ref 9.

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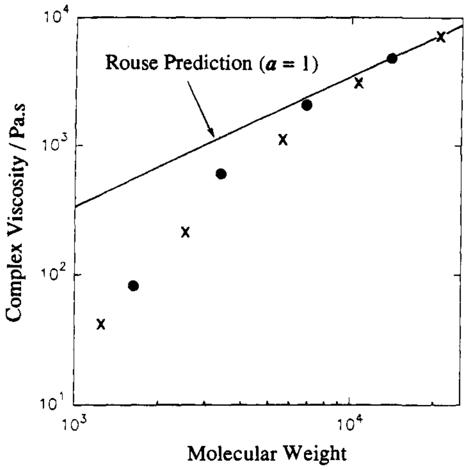

Figure 1. Melt viscosity versus molecular weight for monodendrons (●) and dendritic polyether macromolecules (×), based on 3,5-dihydroxybenzyl alcohol, at 80 °C.

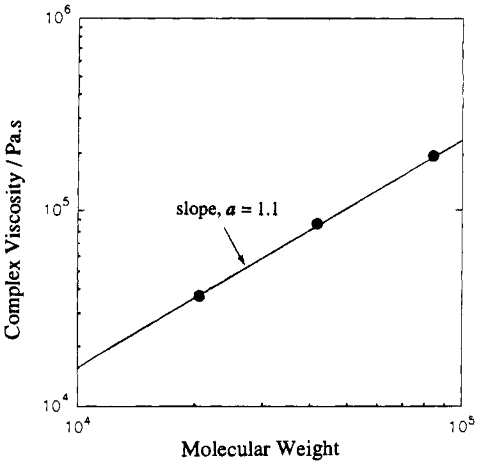

Figure 2. Melt viscosity versus molecular weight for dendritic polyether macromolecules, based on 3,5-dihydroxybenzyl alcohol building blocks and hypercores, at 80 °C.

number of the dendrimer. Significantly, the Rouse prediction of a straight line with a slope, *a*, of 1.0 is not observed. The data actually follows a curve, and only at molecular weights above 10 000 amu does the slope of the plot approach a value of 1.0. This is in partial agreement with the limited number of studies on the melt viscosity of low molecular weight linear polymers in the nonentangled regime.[12-14] For poly(methyl methacrylate), a value for M_c of 10 500 amu is obtained[12] and below a molecular weight of 5000 amu a similar divergence from a linear relationship is observed.[13] The authors attributed this behavior to the Rouse model's assumption of a constant free volume for the melt which breaks down at low molecular weights. However, the main feature of Figure 1 is the absence of a sharp increase in the value of *a* from 1.0 to 3.4 as the molecular weight increases. This lack of a critical molecular weight, M_c, for polyether dendrimers with molecular weights up to 20 000 amu is consistent with the premise that for dendritic macromolecules, unlike most other polymers, including star polymers,[15] chain entanglements are not a dominant feature.

Unfortunately, the synthetic difficulties encountered in the preparation of high molecular weight regular dendrimers by a stepwise convergent growth approach are such that it is difficult to prepare large amounts of high-generation dendrimers. Therefore, an analogous system was prepared using polyphenolic hypercores which allowed the melt viscosity behavior of dendritic macromolecules at higher molecular weights to be investigated. These materials are based on the same fourth-generation dendritic fragment based on **1**, but are coupled to a highly branched, highly functionalized hypercore, prepared from 4,4-bis(4′-hydroxyphenyl)pentan-1-ol, containing either 6, 12, or 24 phenolic groups. The nominal molecular weights of $[G\text{-}4]_6\text{-}[C]$, $[G\text{-}4]_{12}\text{-}[C]$, and $[G\text{-}4]_{24}\text{-}[C]$ are 20 712, 41 881, and 84 220, respectively and the materials are essentially monodisperse. A logarithmic plot of melt viscosity versus molecular weight for the hypercore series is shown in Figure 2. In this case a straight line with a slope of ca. 1.1 is obtained, and the expected increase in the value of *a* is again not observed. This lack of a critical molecular weight, M_c, even at molecular weights approaching 100 000 amu, confirms that the melt viscosity behavior of such regular dendritic macromolecules is not dominated by entanglements. This result is fully consistent with a globular highly branched structure with an increasingly congested surface lacking intermolecular chain entanglements and demonstrates yet another important property variation between dendrimers and normal linear polymers. It should be noted that the melt viscosity values for the second series of dendritic macromolecules are slightly displaced with respect to the first series. This is related to the higher glass transition temperatures for the hypercore series ($T_g(\infty) = 321$ K) when compared to the first series ($T_g(\infty) = 315$ K) and the fact that all experiments were conducted at 80 °C.[5a]

In conclusion, the melt viscosity behavior of dendritic macromolecules has been investigated for the first time. For a family of dendritic polyether macromolecules based on 3,5-dihydroxybenzyl alcohol, the melt viscosity is primarily a function of molecular weight. Examination of the variation in melt viscosity with molecular weight has revealed a unique profile with no critical molecular weight, M_c, being observed with molecules having a molecular weight as high as 85 000 amu. At high molecular weights, a value for *a* of ca. 1.1 is obtained, which is consistent with the premise that branching and surface congestion prevent significant entanglements between separate dendritic macromolecules resulting in "ball-bearing-like" molecules capable of only interdigitation and not true entanglements. We are currently extending this work to the study of the melt viscosity behavior of hybrid linear–dendritic macromolecules.

Acknowledgment. Support of this research by the Australian Research Council, IBM Corporation, and the National Science Foundation (DMR-9224421) is acknowledged with thanks.

JA9500466

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