

Rheology of Concentrated Solutions of Hyperbranched Polyesters

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Abstract

The solution rheology of different generations of hyperbranched polyesters in N-methyl-2-pyrrolidinone (NMP) solvent was examined in this study. The solutions exhibited Newtonian behavior over a wide range of polyester concentrations. Also, the relative viscosities of poly(amidoamine) (PAMAM) dendrimers in ethylenediamine were compared to those of the hyperbranched polyesters in NMP. Both types of dendritic polymers have relative viscosities that are exponential functions of their molar fraction in solution. The slopes of these relative viscosity curves show a linear relationship with respect to the generation number. PAMAM dendrimers have the greater slopes for each generation, reflecting their relatively larger intrinsic viscosity values.

Keywords: Hyperbranched polymer, rheology, dendritic polymer

Introduction

There has been considerable research interest in exploiting the unique molecular architecture of dendrimers and hyperbranched polymers for technological applications (1-4). One such area focuses on utilizing dendritic polymers as rheology modifiers (5). The rheological properties of dendrimers have been more widely studied than those of hyperbranched polymers. However, hyperbranched polymers are more attractive than dendrimers for potential applications as rheology modifiers and processing aides (1-4) because of their relatively easier synthesis route. Dendrimers can be synthesized by either the convergent or divergent approach resulting in nearly monodisperse polymers, and synthesis of several dendritic molecules have been reported [6,7]. However, these syntheses typically require many tedious steps. On the other hand, large quantities of hyperbranched polymers can be easily synthesized in a one-pot reaction from the polycondensation of AB_x monomers, where A and B are different functional groups and x is the functionality of the B group (8). The hyperbranched polymers often lack the monodispersity of dendrimers as they include linear units in their molecular structure. However, such differences do not seem to suppress their typical dendritic polymer characteristics (9).

Many of the rheological studies on dendritic polymers have focused on characterizing their intrinsic properties through solution viscometry or their melt properties. The melt viscosity of several dendrimers (10-13) did not exhibit the characteristic shift in slope when plotted as a function of molecular weight on a logarithmic scale. For linear polymers, this shift in the slope is usually associated with the onset of physical entanglements. At low molecular weights, the zero-shear viscosity, η_0 , scales with molecular weight, M_w , as $\eta_0 \sim M_w$. At high molecular weights, the relationship becomes $\eta_0 \sim M_w^{3.4}$. The melts of dendrimers did not show such a shift in the scaling relationships, but rather a gradual decrease in the slope for increasing molecular weight. This suggests that the dendrimer systems do not contain physical entanglements. The melt viscosity of a hyperbranched polyester (13) also did not show the characteristic shift in slope, although the data represented a narrow molecular weight range.

There have also been a few studies characterizing the solution rheology of dendritic polymers. Uppuluri et al. (10) found that poly(amidoamine) (PAMAM) dendrimers in ethylenediamine exhibited Newtonian behavior under steady shear over a wide range of concentrations and temperatures. Similar Newtonian behavior was found for 50 wt% poly(propyleneimine) (PPI) and acetyl functionalized PPI dendrimers in water (14). However,

Sendjarevic and McHugh (13) reported that poly(ether-imide) (PEI) hyperbranched polymers in 1,2-dichlorobenzene showed shear-thinning behavior for certain concentrations and degrees of branching. The authors attributed this behavior to the presence of physical entanglements in the solution. This represented the first evidence that dendritic polymers exhibited non-Newtonian behavior under steady shear.

In this study, we characterize the solution rheology of four hyperbranched polyester generations in N-methyl-2-pyrrolidinone (NMP) solvent. We develop scaling relationships involving solution viscosity with molar fraction and generation number. We also compare the solution rheology of PAMAM dendrimers (10) with our hyperbranched polymers in terms of the scaling relationships.

Experimental

The hyperbranched polyesters used in this study were donated by Perstorp Inc. (Perstorp, Sweden) and used as received without further purification. These hyperbranched polyesters, the chemical structure of which are presented in Figure 1, were prepared using a single-step condensation reaction of 2,2-dimethylolpropionic acid about a pentaerythritol core. The molecular weights and functionalities of the various polyester generations are given in Table 1. The N-methyl-2-pyrrolidinone solvent was purchased from Aldrich Chemicals and used as received.

Table 1. Properties of various polyester hyperbranched polymers.

Property	G 2	G 3	G 4	G 5
Nominal Mol Wt.	1750	3570	7250	14600
Polydispersity*	1.3	1.5	1.8	2.5
Functionality	16	32	64	128

* Polydispersity was determined by Gel Permeation Chromatography (GPC) using a series of polyethylene oxides as molecular weight standards. Data supplied by manufacturer.

All rheological measurements were made on a Rheometrics Dynamic Stress Rheometer (DSR II) using either cone and plate or Couette geometry. The cone and plate had a 40 mm

diameter and a cone angle of 0.04 radians. The Couette had a 31.9 mm diameter and included a 29.5 mm diameter bob that was 44.25 mm long. All measurements were conducted at 25°C.

Results and Discussion

All the hyperbranched polyester generations in NMP at the various concentrations studied exhibited Newtonian behavior under steady shear. Their viscosities remained constant over shear rates spanning several orders of magnitude (15). Figure 2 shows a typical plot of viscosity as a function of shear rate for solutions of the hyperbranched polyesters of generations 4 and 5 in NMP. The solution remained Newtonian even for concentrations as high as 50 wt.% polymer. Previous studies have also reported Newtonian behavior for dendritic polymer solutions and melts. For instance, Uppuluri et al. (10) found that PAMAM dendrimers in ethylenediamine also exhibited Newtonian behavior over a wide range of concentrations and temperatures. Bulk PAMAM dendrimers also displayed Newtonian behavior under steady shear (11). However, under dynamic oscillatory shear, the complex viscosity values decreased at higher frequencies of oscillation. The authors attributed this behavior to possible intermolecular interactions, such as hydrogen bonding, between the dendrimer molecules or to the proximity of the dendrimers' glass transition temperatures to the experimental temperatures. Another study found that bulk poly(propylenimine) dendrimers end-capped with amine and nitrile groups as well as bulk hyperbranched polyesters displayed Newtonian behavior under steady shear (13). However, in the same study, PEI hyperbranched polymers in 1,2-dichlorobenzene showed shear-thinning behavior. The shear-thinning depended on the solution's concentration and the hyperbranched polymer's degree of branching. The authors explained this behavior by suggesting that entanglements between PEI polymers may be present in the solutions. Note that the PEI polymers had molecular weights more than 3 times those of our highest generation hyperbranched polyester. It seems that hyperbranched polymers do entangle above a certain molecular weight, although this assessment requires confirmation.

The relative viscosities of the different hyperbranched polyester generations do not vary much at constant weight fractions. This is shown in Figure 3, where the viscosities of the hyperbranched polyesters relative to NMP are plotted as a function of weight fraction of the polymer in solution. The lower generations have lower viscosities, but the viscosity differences are not great. This can be attributed to the differences in molar concentrations at a specific

weight fraction and the differences in intrinsic viscosities of the different generations. For a certain weight fraction, there are fewer moles of the higher molecular weight, or higher generation, polyesters. This should result in lowering the relative viscosity of the higher generation samples compared to the lower generation samples. However, the higher generations have larger intrinsic viscosities and, consequently, should have larger relative viscosities. These two factors appear to be of comparable magnitudes and apparently balance each other at the various weight fractions.

When the viscosities are plotted in terms of molar rather than weight fractions (see Figure 4), the disparity of viscosities between different generations becomes readily apparent. At large molar fractions, generation 5 polyesters have relative viscosities several orders of magnitude greater than those of lower generation samples. A molecular-level explanation for this interesting observation might be based on the possible interaction of the terminal chains at the periphery of the dendritic molecules being primarily responsible for the viscous behavior. Unlike with linear polymers, the number of chain ends available for entanglement in dendritic molecules is not directly proportional to the weight fraction at different molecular weights. It is the molar fraction that is proportional to the number of peripheral chain ends in dendritic molecules. Thus in this instance a dependence of the relative viscosity on molar concentration is not unexpected. However, the concentration dependence of viscosity, when plotted as a function of the molar concentration of chain ends (i.e., the molar concentration of the terminal [OH] functionalities), must be generation independent. This is illustrated to be the case in Figure 5.

Another interesting feature of Figure 4 is that the log viscosity plots are linear for each generation, suggesting that the data can be fitted with an exponential function. When we plot the PAMAM dendrimer data (10) in a similar fashion in Figure 4, the relative viscosity data for each generation also appear to be linear. However, the slopes of the PAMAM dendrimer curves for a given generation are greater than those of the hyperbranched polyester curves. The larger slopes of the PAMAM dendrimer curves compared to those of the hyperbranched polyester curves (Figure 4) reflect the PAMAM dendrimer's larger intrinsic viscosity or hydrodynamic radius for each generation. Figure 6 presents a plot of the relative viscosity's slopes for the two dendritic polymers as a function of the functionality Z (i.e., the number of OH functionalities per molecule).

Conclusions

The four generations of hyperbranched polyesters in NMP exhibited Newtonian behavior under steady shear over the concentration range examined in this study. The relative viscosities of the polyesters of different generations did not vary much at specific weight fractions. However, when the relative viscosity was plotted as a function of molar fraction of the dendritic polymer, the solution viscosities were seen to be clearly concentration dependent. For a specific weight fraction of the polymer there are fewer moles of the higher generation polyesters in solution. At a specific molar fraction, however, equimolar solutions of the polymer do show large differences in viscosity as the higher generation larger molecules they should have considerably greater relative viscosities than the smaller molecules of lower generation.

Plots of the relative viscosity as a function of the concentration of terminal chains (regardless of the generation) are about the same for all generations. This supports the possibility that it is the interaction of the terminal chains that is responsible for the viscosity in these systems.

The relative viscosities of the hyperbranched polyesters from present investigation were compared to those reported for PAMAM dendrimers. The logarithm of the relative viscosities of both dendritic polymers as a function of molar fraction yielded linear plots. We also found a linear relationship when we plotted the slopes of those viscosity curves as a function of the generation. For each generation, the PAMAM dendrimers have larger slopes, reflecting their relatively larger intrinsic viscosity or hydrodynamic radius values compared to the hyperbranched polyesters studied here.

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FIGURES

Figure 1: Chemical structure and synthesis procedure for hyperbranched polyesters.

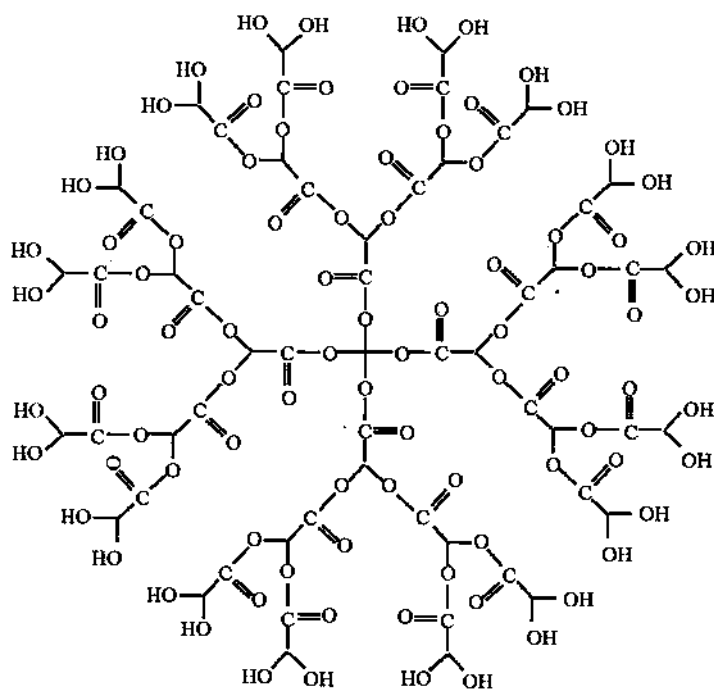
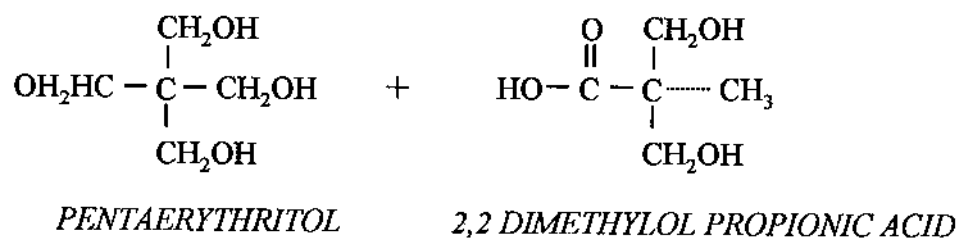
Figure 2: Viscosity as a function of shear rate for 50 weight percent solutions of hyperbranched polyesters in NMP.

Figure 3: Relative viscosity of the hyperbranched polymers as a function of their weight fraction in solution.

Figure 4: Relative viscosity of the hyperbranched polymers as a function of their molar fraction in solution.

Figure 5: Relative viscosity of hyperbranched polymer as a function of the molar fraction of terminal chain ends.

Figure 6: Slopes of the plots of relative viscosity versus molar fraction for PAMAM dendrimers and hyperbranched polymers as a function of functionality.



Idealized hyperbranched polyester

Figure 1.

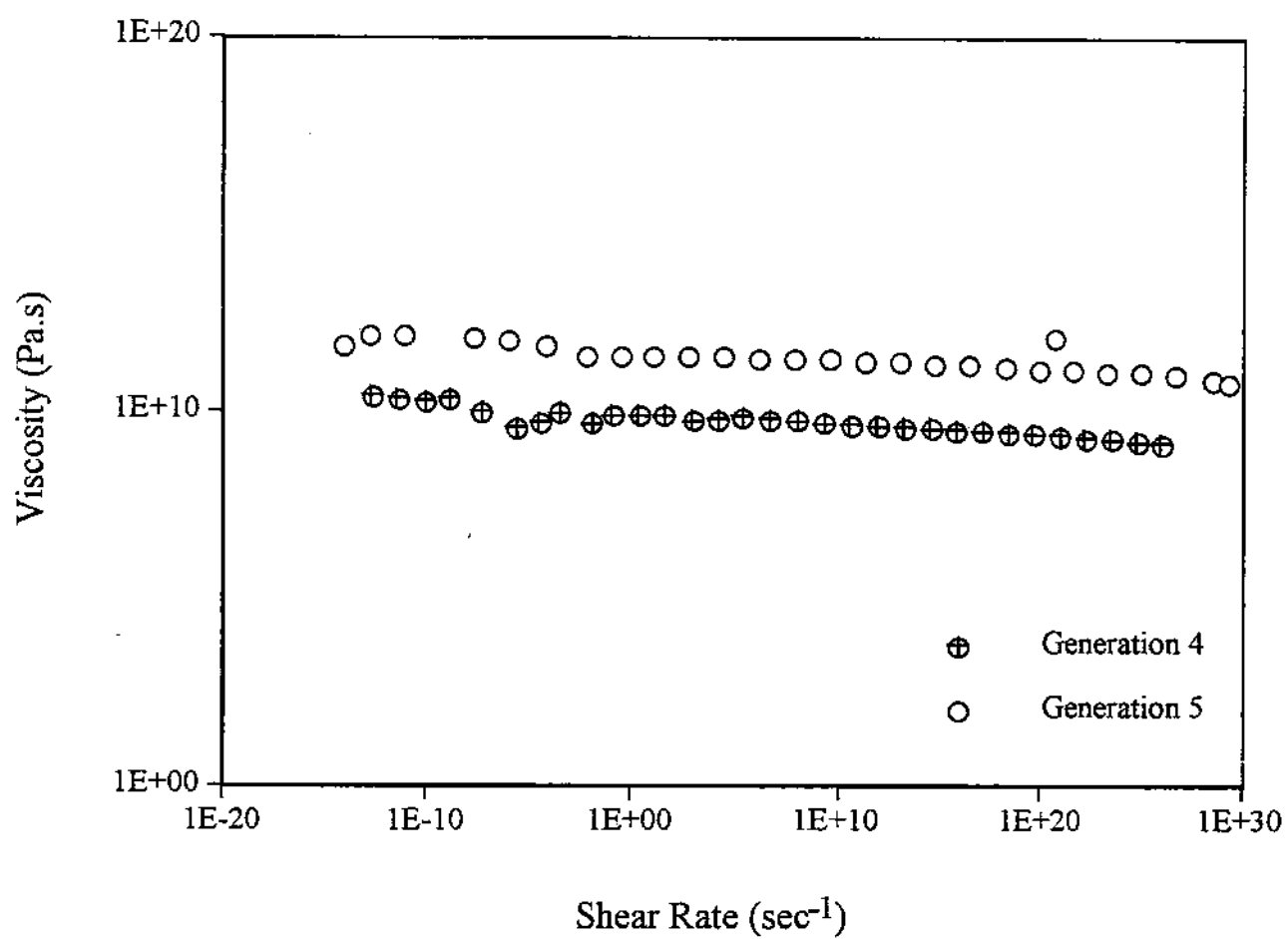


Figure 2.

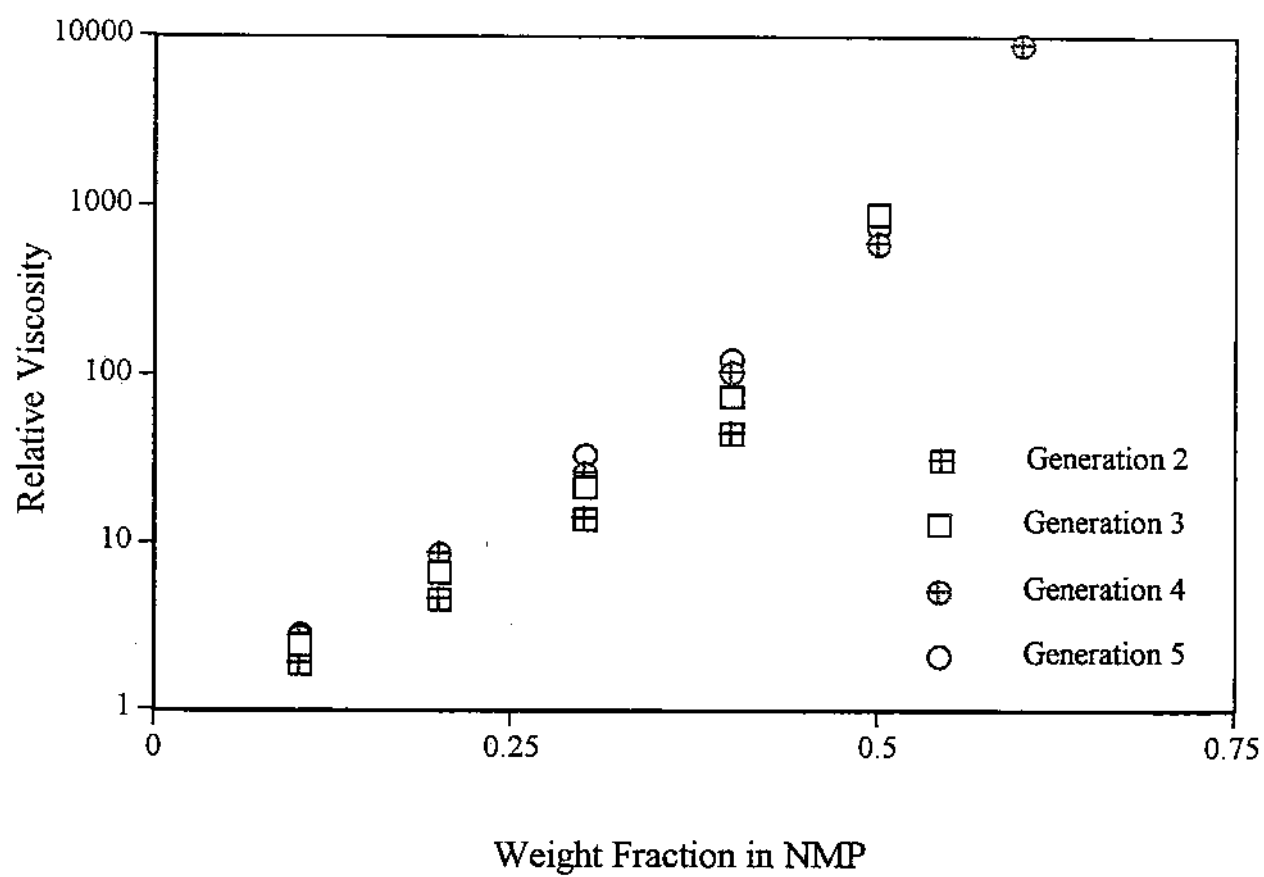


Figure 3.

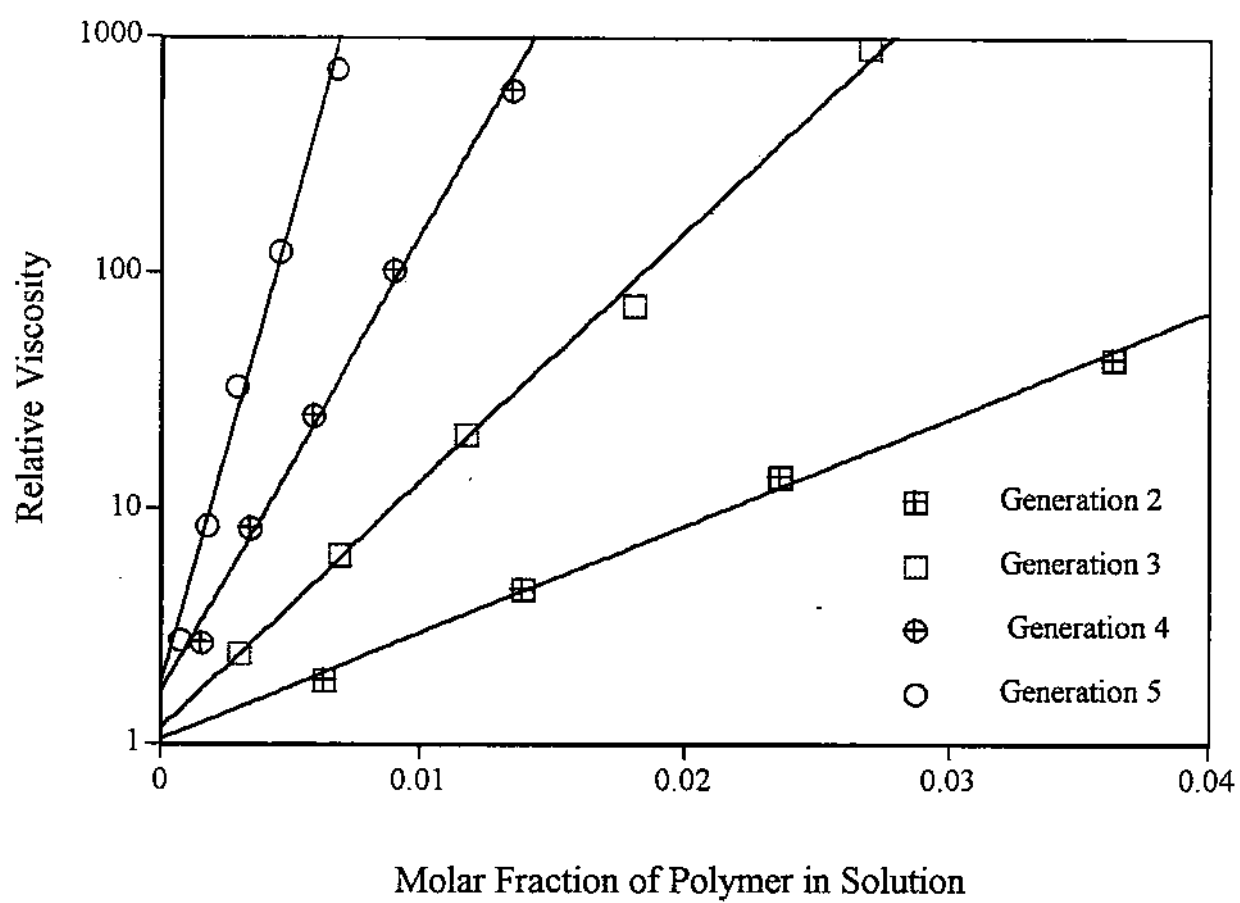


Figure 4.

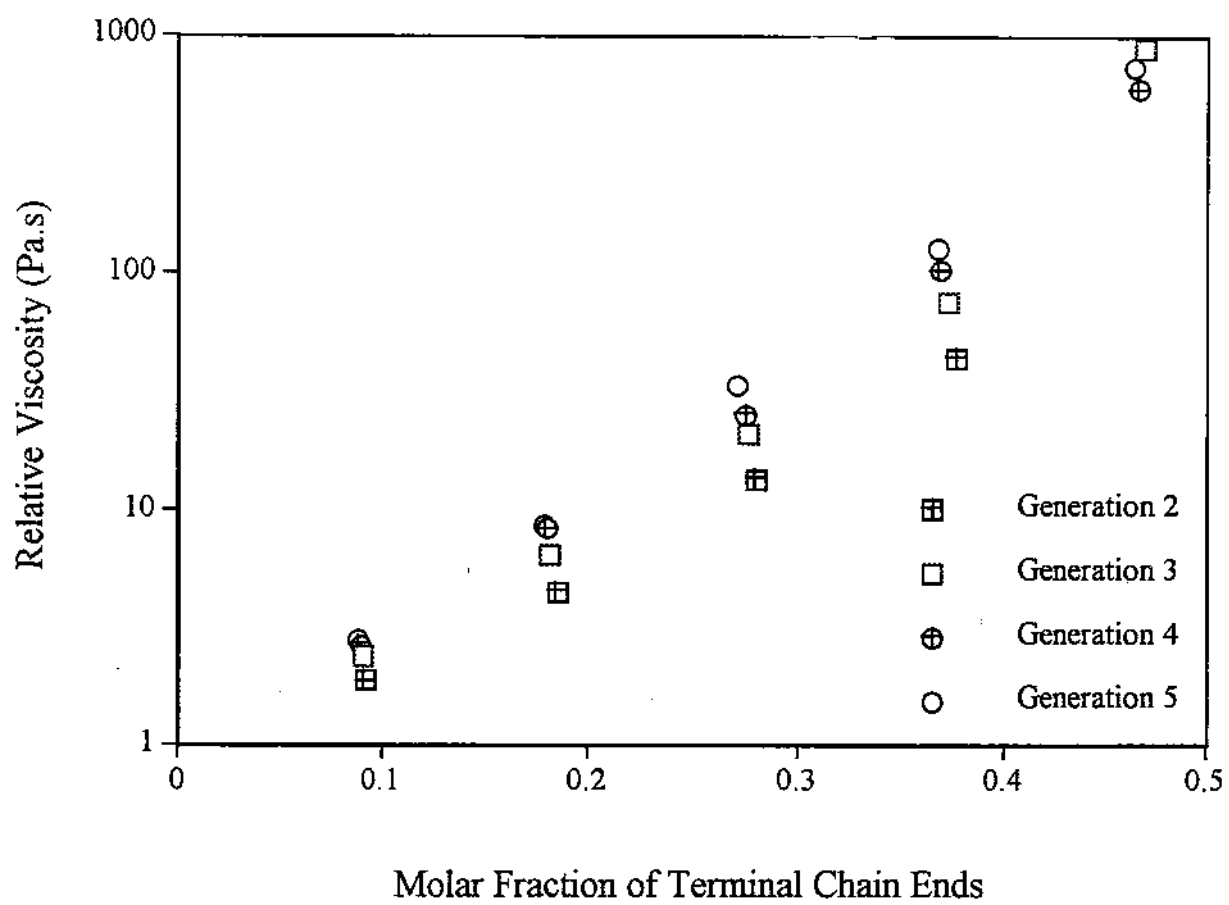


Figure 5.

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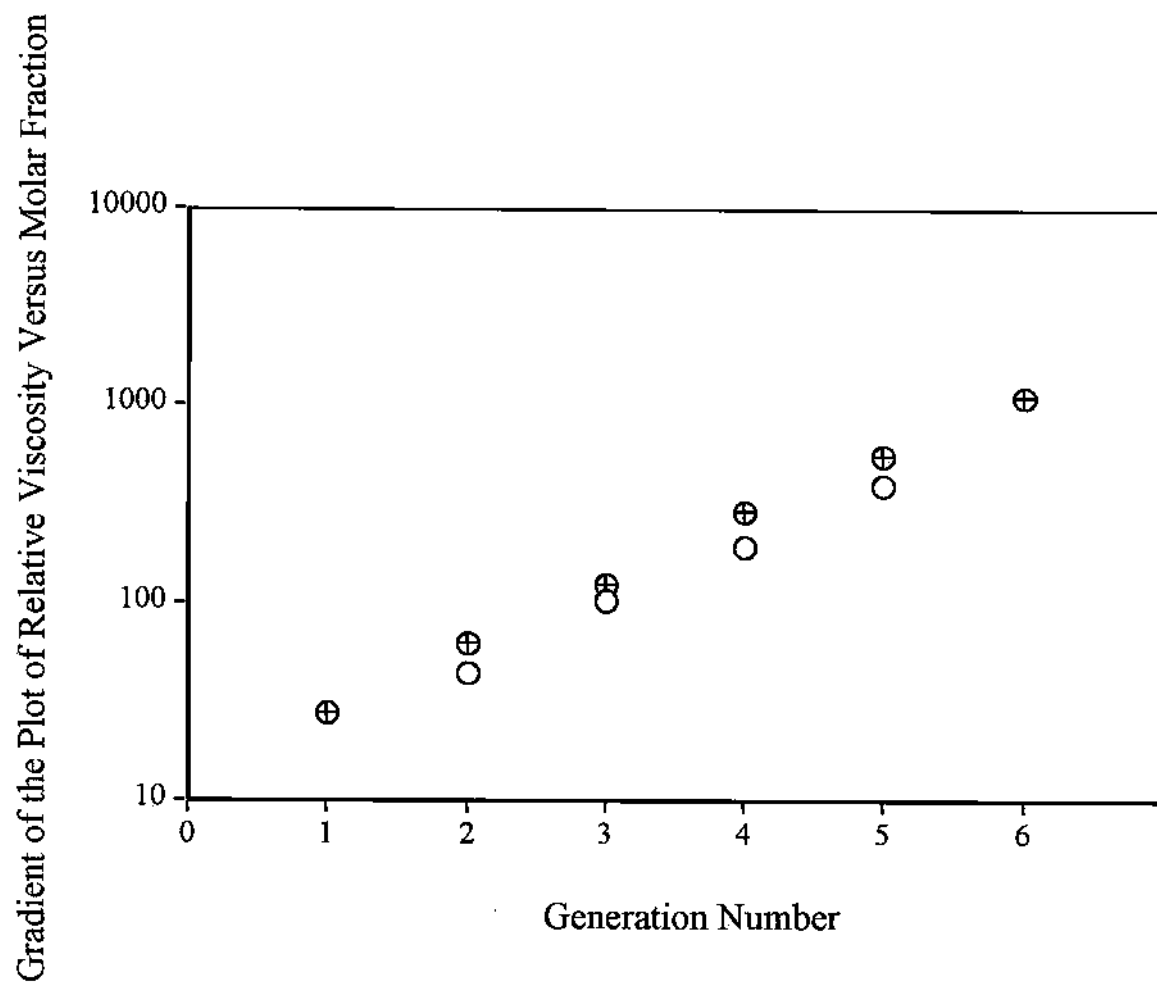


Figure 6.