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Solution Rheology of Hyperbranched Polyesters and Their Blends with Linear Polymers

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ABSTRACT: The rheological properties of different generations of hyperbranched polyesters in 1-methyl-2-pyrrolidinone solvent and their blends with a poly(2-hydroxyethyl methacrylate) are examined in this study. All the hyperbranched polyester solutions exhibit Newtonian behavior, with steady shear viscosities independent of shear rate. This indicates the absence of physical entanglements in these systems. In addition, solution viscosities are found to be only slightly affected by the different generations of the hyperbranched polymer. The polyesters have very small intrinsic viscosities, and their hydrodynamic radius scales as $R_h \sim M^{0.39}$, suggesting a less packed structure than dendrimers. All generations of the hyperbranched polyesters also show comparable apparent activation energies of flow over the temperature range studied. Replacing linear polymers with hyperbranched polymers causes large reductions in the blend viscosities. This behavior can be attributed to the decrease in both the number of physical entanglements between linear polymers and the blend's intrinsic viscosity upon addition of the hyperbranched polymer.

Introduction

The unusual solution properties and molecular architecture of dendritic polymers have made them attractive candidates for use as rheology modifiers.[1] In using the term dendritic polymers, we include both dendrimers and hyperbranched polymers. They possess strikingly low intrinsic viscosities and very high solubilities compared to those of linear polymers.[2] The low intrinsic viscosity is due to their packed structure, while the high solubility is a result of the large number of peripheral terminal functional groups available per macromolecule. These properties allow large amounts of dendritic polymers to be added to polymeric blends and formulations without leading to a large increase in their viscosity.

Most rheological studies on dendritic polymers have focused on characterizing their intrinsic properties through dilute solution viscometry.[3,4] There have been very few studies examining the concentrated solution or melt properties of these polymers.[5,6] In addition, the more detailed and rigorous studies have involved dendrimers and not hyperbranched polymers. These studies have found that dendrimer solutions with concentrations as high as 75 wt % still exhibit Newtonian behavior.[5] Dendrimer melts also do not show the characteristic slope change in zero-shear viscosity when plotted as a function of molecular weight on a logarithmic scale.[5,6] These results indicate that no physical entanglements are present in these systems.

There have also been very few studies examining dendritic and linear polymer blends.[7−9] None of these have involved detailed rheological characterizations of the blends. Instead, they have focused more on the synthesis of various types of hyperbranched polymers,[7] the phase behavior of the blends,[8] or the dynamic mechanical and tensile properties of the blends.[9] One study[7] found that, for several blends of linear and hyperbranched polymers, the one containing a higher concentration of hyperbranched polymers had a lower viscosity.

While dendrimers have been more widely studied, hyperbranched polymers rather than dendrimers are of greater interest from an application standpoint. These materials are based on polymerizations of AB_x monomer systems,[10] where A and B are different functional groups and x is the functionality at the B group. They are relatively inexpensive to produce and, unlike dendrimers, are easy to synthesize in large quantities. The hyperbranched polymers lack the near-monodispersity of dendrimers and include some linear units in their molecular structure. A small-angle X-ray scattering study[11] has shown that hyperbranched polymers have a wider distribution of sizes and shapes than the spheroid shape of dendrimers. However, these differences in hyperbranched polymers do not seem to be large enough to suppress their typical dendritic polymer characteristics.[2]
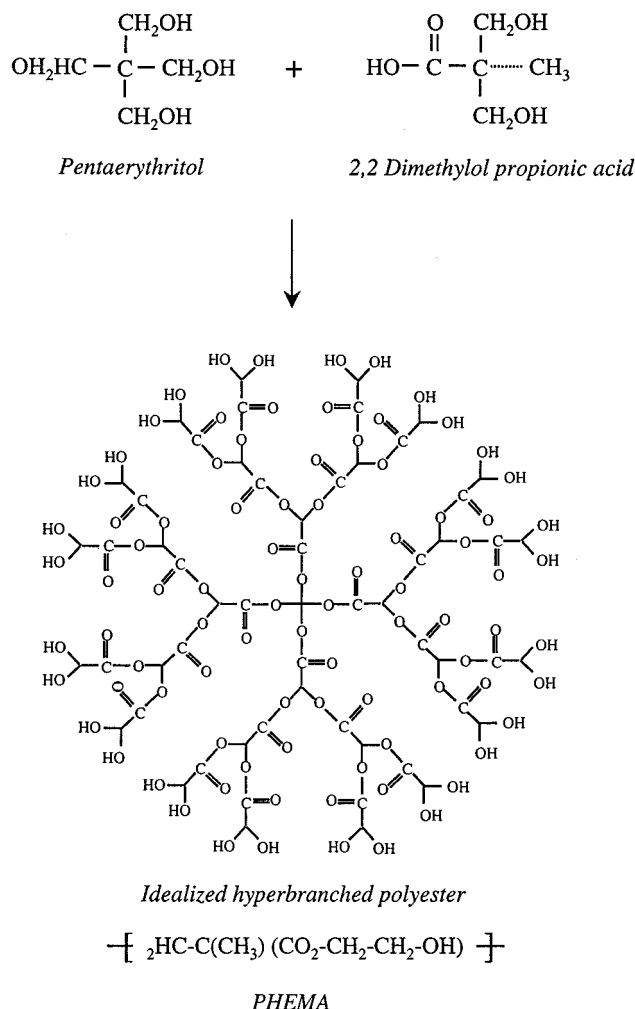
The primary focus of the present study is to investigate the rheology of concentrated solutions of hyperbranched polyesters and their blends with a high molecular weight linear polymer, poly(2-hydroxyethyl methacrylate) (PHEMA). The emphasis on fairly concentrated solutions and the use of high molecular weight linear polymer stems from our particular interest in using hyperbranched polymer blends for coating applications. Typical coating applications require high molecular weight polymers but low viscosities. These mutually exclusive requirements may be possible through use of linear polymers in combination with hyperbranched polymers. In this study, we use model systems

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Pentaerythritol   *2,2 Dimethylol propionic acid*

Idealized hyperbranched polyester

$$-\!\!\!\left[\!\!\!_2HC\text{-}C(CH_3)\,(CO_2\text{-}CH_2\text{-}CH_2\text{-}OH)\,\right]\!\!\!-$$

PHEMA

Figure 1. Idealized structures for hyperbranched polyesters (G3) and linear PHEMA.

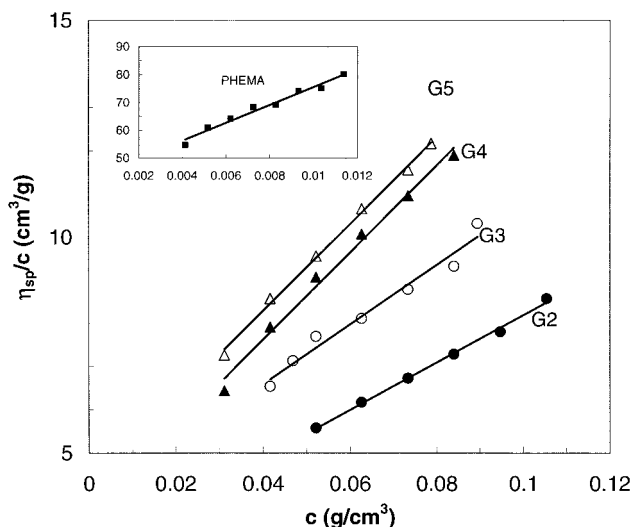**Table 1. Physical Properties of Hyperbranched Polyesters**

property	G2	G3	G4	G5
nominal mol wt	1750	3570	7250	14600
functionality	16	32	64	128
polydispersity	1.3	1.5	1.8	2.5

to examine the concentration-dependent viscosity of hyperbranched polyesters of up to five generations, the solution blend viscosity at different blend compositions, and the effects of temperature on viscosity of the hyperbranched polymer solutions.

Experimental Section

Sample Preparation. The hyperbranched polyesters were provided by Perstorp, Inc. (Perstorp, Sweden), and were used as received without further purification. The hyperbranched polyesters were prepared using the divergent approach in a single-step condensation reaction of 2,2-dimethylolpropionic acid about a core of Pentaerythritol. Hyperbranch growth was controlled via the stoichiometric ratio of the core to the monomers. Figure 1 summarizes the chemical structure and synthetic approach used in their manufacture. The molecular weights and functionalities of the various generations of the polyesters are given in Table 1.

PHEMA was purchased from Aldrich Chemicals and used as received. Its chemical structure is shown in Figure 1, and it has an average M_v of 300 000. A high molecular weight polymer was chosen because coating formulations contain high molecular weight species. The solvent, *N*-methyl-2-pyrroli-

Figure 2. Huggins plots for hyperbranched polyesters of different generations (G2–G5) and PHEMA used in determining intrinsic viscosities. Here, η_{sp} is the specific viscosity and c is the concentration.

dinone (NMP), was also purchased from Aldrich Chemicals and used as received. The hyperbranched polyester solutions were prepared by mixing the polymer and NMP with a stir bar for several hours. The polyester/PHEMA blends were prepared by initially dissolving PHEMA in the NMP. This sample was mixed with a stir bar for several hours until the linear polymer dissolved. The hyperbranched polyesters were then added, and the sample was mixed for several more hours. The concentrations (weight percent) of polymers used in this study were based on the weight of the polymers divided by the total weight of the sample.

Rheological Characterization. A Rheometrics Dynamic Stress Rheometer (DSRII) was used to measure the viscosity of all samples. Two types of geometries were used, depending on the viscosity of the sample. For low viscosities, a 31.9 mm diameter couette geometry with a 29.5 mm diameter bob 44.25 mm long was utilized. For high viscosities, a 40 mm diameter cone and plate geometry with a cone angle of 0.04 rad was utilized. Intrinsic viscosities of the hyperbranched polymers and PHEMA were determined by using the Huggins equation[12] and plotting η_{sp}/c as a function of c, where η_{sp} is the specific viscosity and c is the concentration. Extrapolation of the data to zero concentration yielded the intrinsic viscosity, $[\eta]$. Figure 2 shows the Huggins plots for the linear and hyperbranched polymers.

Results and Discussion

Hyperbranched Polyesters in NMP. All the hyperbranched polyester samples in NMP exhibited Newtonian behavior, even at high concentrations. Typical plots of viscosity as a function of shear rate are shown in Figure 3 for several concentrations of generation 5 polymers. The viscosities are independent of shear rate, in contrast to high molecular weight linear polymers or colloidal particles, which may exhibit non-Newtonian shear thinning or shear thickening behavior. Poly-(amidoamine) (PAMAM) dendrimers in ethylenediamine solutions were recently reported[5] to show similar Newtonian behavior over a wide range of concentrations and temperatures. Despite their irregularities in molecular architecture, hyperbranched polyesters behave like dendrimers in solution and display Newtonian behavior.

The solution viscosities of hyperbranched polyesters also show only a slight dependence on generation number (and hence on the average molecular weight), much like dendrimer solutions.[8] Figure 4 compares the
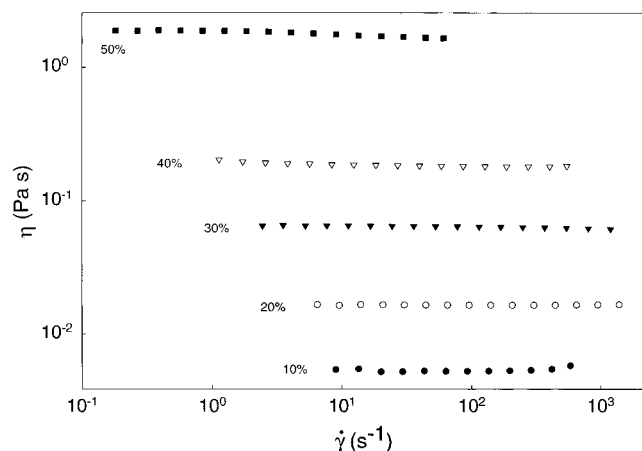
Figure 3. Viscosity as a function of shear rate for hyperbranched polyesters of generation 5. The concentrations are in terms of weight percent.
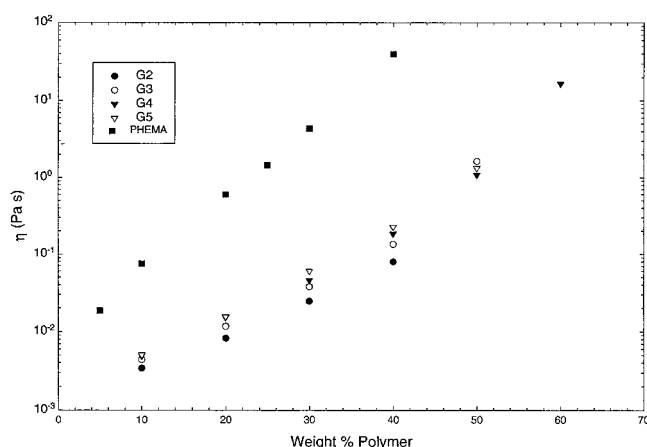
Figure 4. Comparison of the zero-shear viscosities of the linear PHEMA polymer with the various hyperbranched polyesters.

viscosities of the different generations at various concentrations. The general trend seems to indicate that the higher generation polymers yield slightly higher solution viscosities. Their behavior in this regard is also similar to that of "star" polymers, such as star polyisobutylenes, where the dilute solution viscosities of the polymers were reported to be relatively independent of the molecular weight of the star polymer.[13]

The absolute values of solution viscosity for hyperbranched polyesters were much smaller than those for the higher molecular weight PHEMA in the same solvent. This behavior can be seen in Figure 4. The difference in viscosities between PHEMA and hyperbranched polyesters can be attributed to several factors. One factor is the absence of chain entanglements between the hyperbranched polymers. Another factor is that hyperbranched polyesters have much lower intrinsic viscosities than PHEMA, due to their relatively lower molecular weights and denser structures when compared to PHEMA.

Several features of the hyperbranched polymer structure contribute to the absence of chain entanglements. First, they have a globular shape with a highly branched structure composed of short chain segments (of dimethylolpropionic acid condensate for the hyperbranched polyesters in this study), which are much smaller than the critical molecular weights at which linear polymers typically show entanglement effects. In addition, com-

Table 2. Intrinsic Viscosity and Hydrodynamic Radius of Polymers[19]

polymer	$[\eta]$ (cm³/g)	R_h (Å)	polymer	$[\eta]$ (cm³/g)	R_h (Å)
generation 2	2.70	9.08	generation 5	4.24	21.4
generation 3	3.80	12.9	PHEMA	44.7	129
generation 4	3.55	16.0			

puter simulation[14-17] and theoretical[18] studies have shown that peripheral chains, which might participate in entanglements, appear to be able to fold back into the interior of the globular polymer. Consequently, these chains are no longer able to interact with other polymer molecules. The absence of entanglements has been observed in several studies on dendrimers,[5,6] where the logarithmic plots of zero shear viscosity as a function of molecular weight under melt conditions did not exhibit the characteristic break associated with entanglements.

Hyperbranched polyesters also have very small intrinsic viscosities compared to that of PHEMA. This is evident from the intrinsic viscosity values obtained from the Huggins plot (Figure 2) and tabulated in Table 2. The hyperbranched polyesters have intrinsic viscosities an order of magnitude lower than for the linear PHEMA due to the higher molecular weight of PHEMA, as well as the highly branched structure of the polyesters. Intrinsic viscosity measures the ratio of hydrodynamic volume to molecular weight. Hyperbranched polymers have more densely packed structures, resulting in smaller hydrodynamic volumes compared to those of linear polymers with comparable molecular weights. In a shear field, the larger object dissipates more energy, resulting in a higher viscosity. Consequently, PHEMA's larger hydrodynamic volume would naturally lead to a higher viscosity.

The hyperbranched polyesters show a trend of increasing intrinsic viscosity with generation number (see Table 2). However, the generation 3 polymer seems to have a slightly larger intrinsic viscosity than the generation 4 polymer. We are not sure of the reason for this behavior, although we suspect that it may be due to the polydispersity of the samples. This trend of increasing intrinsic viscosity is different from that found for some dendrimers, where a maximum in intrinsic viscosity has been observed.[3,19]

Several experimental and computer simulation studies have examined the relationship between dendrimer size and molecular weight. One measure of size is the hydrodynamic radius of a polymer in solution. The hydrodynamic radius can be determined from the intrinsic viscosity by using Einstein's equation for hard spheres:[12]

$$R_h = \left(\frac{3[\eta]M}{10\pi N_A}\right)^{1/3} \qquad (1)$$

where R_h is the hydrodynamic radius, $[\eta]$ is the intrinsic viscosity, M is the molecular weight, and N_A is Avogadro's number. The radius values for the hyperbranched polyesters are calculated by using eq 1 and are tabulated in Table 2. Most studies have obtained power law relationships between the radius of gyration and molecular weight. Since we have hydrodynamic radius instead of radius of gyration values, we need to ensure that the two values are proportional to each other. This was determined to be the case for all generations[17] or for low generation numbers (G < 6).[14] Thus, we can scale
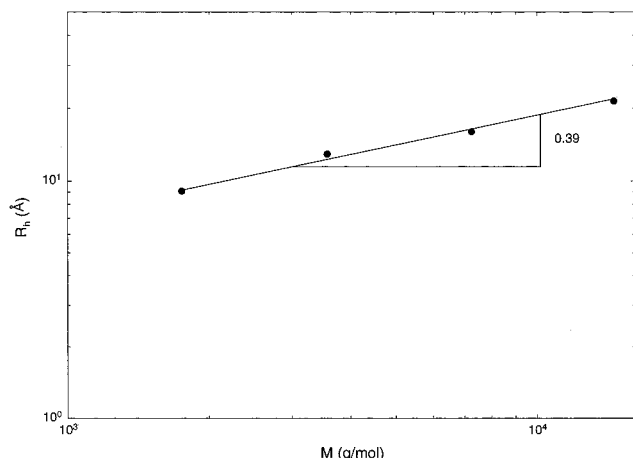
Figure 5. Hydrodynamic radius as a function of the molecular weight of hyperbranched polyesters. A power law fit with an exponent of 0.39 is obtained.

our hydrodynamic radius values with molecular weight and be able to compare them with literature values. Figure 5 shows the power law relationship between the hydrodynamic radius and molecular weight. The radius scales as $R_h \sim M^{0.39}$.

Computer simulation and theoretical studies have shown several different scaling relationships between radius and molecular weight. De Gennes and Hervet[20] used self-consistent-field analysis to determine that the radius scales as $R \sim M^{0.2}$ below the critical point at which imperfect dendritic growth occurred. In a Monte Carlo simulation study, Chen and Cui[14] also found a similar scaling exponent of 0.178 between the end-to-center distance of the dendrimer and the total number of monomers in the molecule. However, other studies have found very different scaling relationships. Lescanec and Muthukumar[16] used a kinetic growth model to determine that $R_g \sim M^{0.5}$ for low M and $R_g \sim M^{0.22}$ for high M, where R_g is the radius of gyration. In a molecular dynamics study of dendrimers under varying solvent conditions, Murat and Grest[15] found that $R_g \sim N^{0.33}$ under all solvent conditions, where N is the number of monomers in the dendrimer. Similar exponent values were determined by Mansfield[21] using Monte Carlo simulations. He found that the dendrimers were fractals over a narrow range of radius values with $R \sim M^{0.362}$ to $R \sim M^{0.408}$ for generations 6 to 9, respectively. This indicated that the structures became more packed at higher generations.

There have been few experimental studies relating radius to molecular weight. The studies which have been done seem to support the exponent values determined by Murat and Grest[15] and Mansfield.[21] In a study involving poly(propyleneimine) dendrimers with two different types of end groups, Scherrenberg et al.[4] found that $R_h \sim M^{0.37}$ for both dendrimers. Stechemesser and Eimer[22] used holographic relaxation spectroscopy to determine $R_h \sim M^{0.33}$ for poly(amidoamine) dendrimers in methanol. Both of these studies involved dendrimers and yielded a slightly smaller scaling exponent than the 0.39 value obtained for the hyperbranched polyesters in this study. Comparing size scales of dendritic polymers with different chemical compositions in different solvents may not be prudent since intramolecular and polymer–solvent interactions may contribute significantly to their conformations. Nevertheless, the larger exponent value for the hyperbranched polymer seems
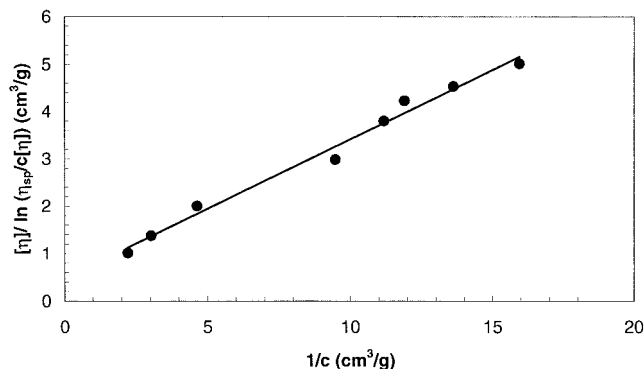
Figure 6. A representative Lyons–Tobolsky plot used to determine the fitting parameters, k_L and b. Data are for generation 3 and show linear behavior for concentrations ranging from 0.063 to 0.450 g/cm³ (6 to 40 wt %).

Table 3. Lyons–Tobolsky Fitting Parameters[25]

generation	k_L	b (cm³/g)
2	5.49	−2.83
3	3.40	−1.61
4	5.41	−3.21
5	3.83	−2.26

to make sense since it indicates a less densely packed structure than the dendrimers. Hyperbranched polymers have imperfect branching and contain linear segments, in contrast to perfect branching found in dendrimers. This imperfection would cause hyperbranched polymers to occupy more space than dendrimers with comparable molecular weight.

Various empirical models have been used to fit viscosity data over a wide range of concentrations for linear and branched polymers.[23,24] However, no studies have examined whether these same equations can be applied to hyperbranched polymers. One such model, which fits linear polymer data well, is the Lyons–Tobolsky equation:[25]

$$\eta_{sp}/c[\eta] = e^{k_L[\eta]c(1-bc)} \quad (2)$$

where η_{sp} is the specific viscosity, c is the concentration, $[\eta]$ is the intrinsic viscosity, and k_L and b are fitting constants. The fitting constants can be determined from experimental data by rearranging eq 2 to obtain

$$\frac{[\eta]}{\ln\left(\dfrac{\eta_{sp}}{c[\eta]}\right)} = \frac{1}{k_L c} - \frac{b}{k_L} \quad (3)$$

A plot of $[\eta]/\ln(\eta_{sp}/c[\eta])$ as a function of $1/c$ should be linear with a slope of $1/k_L$ and an intercept of $-b/k_L$. Such a plot is shown in Figure 6 for generation 3 samples. For all the hyperbranched polymer generations, the plots are linear for concentrations ranging from 0.063 to 0.450 g/cm³ (6 to 40 wt %). The values of k_L and b for each generation are shown in Table 3.

Experimentally determined values of η_{sp}/c for different concentrations are compared to the Lyons–Tobolsky equation in Figure 7. The fit to the experimental data is excellent at lower concentrations, but it starts to break down around 0.450 g/cm³ (40 wt %). After this point, the viscosities are larger than those determined from the Lyons–Tobolsky equation. This equation has been shown to fit viscosity data over the entire range of concentrations for a linear polymer in two different
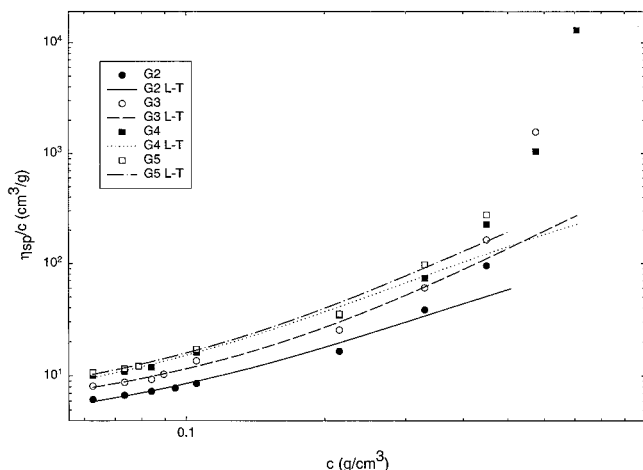
Figure 7. Experimentally determined values of η_{sp}/c compared to a fit involving the Lyons–Tobolsky equation for the various hyperbranched polyesters. Exp refers to experimental data, and L–T denotes the fit of the Lyons–Tobolsky equation. The equation fits the data very well for low concentrations but starts to deviate at around 0.450 g/cm^3 (40 wt %).
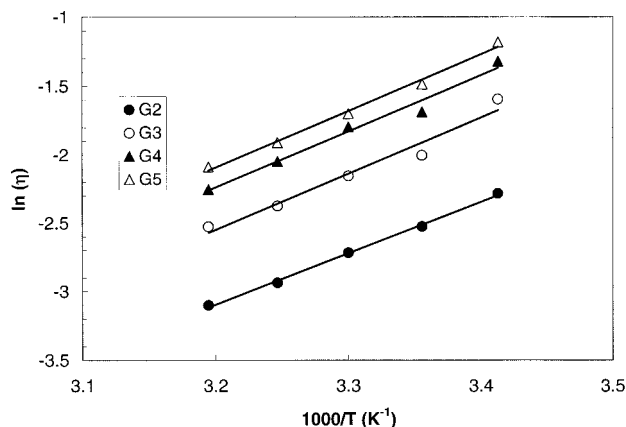
Figure 8. Arrhenius plot of η as a function of inverse temperature to determine the apparent activation energy of flow for the various hyperbranched polyesters. All generations have apparent activation energies of about 8 kcal/mol.

solvents.[25] However, the Lyons–Tobolsky equation was only partially successful for hyperbranched polymers.

Temperature Dependence of Viscosity. The solution viscosities of all hyperbranched polyester generations show similar temperature dependence effects. Figure 8 shows the solution viscosities of the different generations at a fixed concentration of 40 wt % over a temperature range between 20 and 40 °C. The data follow the Arrhenius-type equation[26]

$$\ln(\eta) = A + \frac{E_\eta}{RT} \tag{4}$$

where η is the viscosity, A is the preexponential factor, E_η is the apparent activation energy of flow, R is the gas constant, and T is the temperature. Apparent activation energies of 7.5, 8.2, 8.1, and 8.2 kcal/mol were determined for generations 2–5. These values agree fairly well with the 5–7 kcal/mol values reported for PAMAM dendrimer solutions of similar concentrations.[5]

Hyperbranched Polyester and PHEMA Blends. Blending hyperbranched polyesters with PHEMA results in comparable reductions in viscosity for the different hyperbranched polyester generations. Figure 9 shows the zero-shear viscosity of hyperbranched
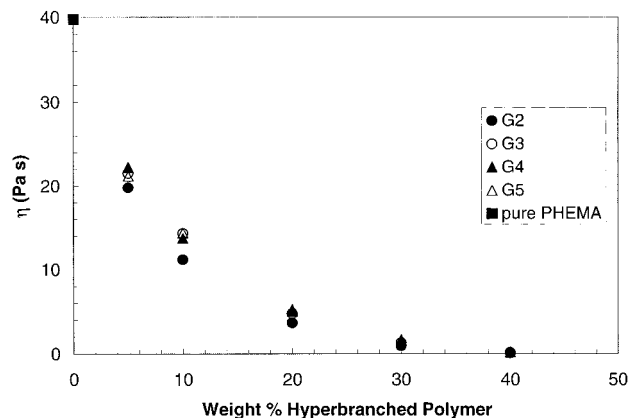

Figure 9. Solution viscosities for blends of hyperbranched polyesters and PHEMA. The viscosity decreases drastically even when small amounts of linear polymers are replaced with hyperbranched polymers. The total polymer content has been kept constant at 40 wt %.

polyester/PHEMA blends in NMP. The total polymer concentration was kept constant at 40 wt %. The results indicate that replacing PHEMA with generation 2 polyesters gives the greatest reduction in viscosity. However, there is not much difference in the viscosity values between the different generations. This is due to the disparity of intrinsic viscosities between the hyperbranched polyester and PHEMA. Compared to the much larger intrinsic viscosity of PHEMA, the polyesters all have relatively similar intrinsic viscosity values (see Table 2). Consequently, the different generation blends exhibit similar viscosities. However, if a linear polymer with a lower intrinsic viscosity were used, the different generations would show a larger range of viscosity values.

The blend viscosity shows a precipitous drop in value when the linear polymer is partially replaced by the hyperbranched polymer. Even when only 5 wt % of the PHEMA has been replaced, the blend viscosity drops by a factor of 2. This effect can be attributed to several factors. First, it is reasonable to expect the globular hyperbranched polymers to disrupt the copious entanglements of linear chains by physically separating them. Physical entanglements are present in the blends because the PHEMA concentrations lie in the semidilute and concentrated regimes. A value of $c[\eta]$ equal to 1 denotes the lower bound value for semidilute solutions while a value of 10 denotes the lower bound value for concentrated solutions.[27] For PHEMA in NMP, the concentrations corresponding to these lower bound values are 2.17 and 21.22 wt %. Since the PHEMA used in this study has a molecular weight well above the critical molecular weight for entanglement, physical entanglements should be present in all the blends. Figure 10 shows viscosity as a function of shear rate for blends containing generation 3 polymers. Slight shear thinning occurs at high shear rates, indicating the presence of physical entanglements. Note that the critical shear rate for shear thinning becomes greater for higher concentrations of hyperbranched polymer. This suggests that introducing hyperbranched polymers to the system results in fewer entanglements.

Another reason for such large decreases in the viscosity when PHEMA is replaced by hyperbranched polymers is again the result of the large disparity between their intrinsic viscosities. PHEMA has an intrinsic viscosity 10 times greater than the largest hyper-
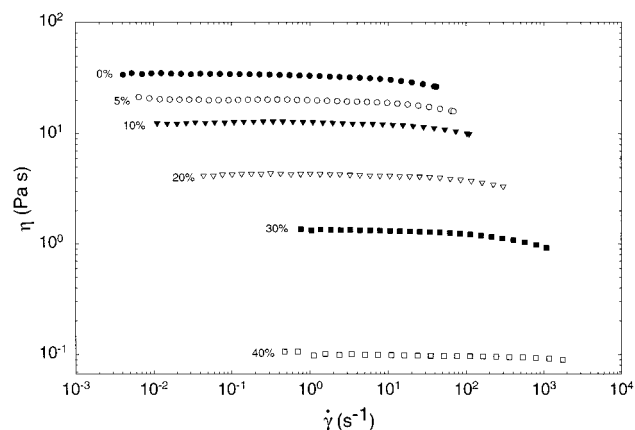
Figure 10. Viscosity as a function of shear rate for generation 3 blends. The concentrations are in terms of weight percent hyperbranched polyester. Shear thinning for higher hyperbranched polymer concentrations occurs at higher shear rates, indicating less physical entanglements in these systems.
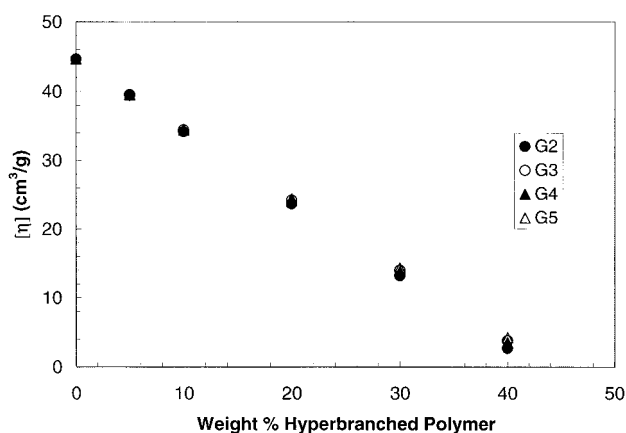
Figure 11. Intrinsic viscosity of blends of PHEMA with hyperbranched polyesters as a function of hyperbranched polyester concentration. The total concentration of polymers has been kept constant at 40 wt %.

branched polymer (see Table 2). The intrinsic viscosities for the blends can be determined by summing the weighted contribution of each component:[12]

$$c[\eta] = \sum_i c_i[\eta]_i \qquad (5)$$

where c is the total concentration of the blend, $[\eta]$ is the intrinsic viscosity of the blend, c_i is the concentration of component i, and $[\eta]_i$ is the intrinsic viscosity of component i. Figure 11 presents the intrinsic viscosities of the blends for different hyperbranched polymer concentrations. This plot shows a monotonic decrease in the intrinsic viscosities with increasing hyperbranched polymer content. From Figure 9, we see that the largest decrease in viscosity occurs when the first 5 wt % of PHEMA is replaced by hyperbranched polymers. The reason for this is the inherently nonlinear relationship between intrinsic and zero-shear viscosity. For example, the Lyons−Tobolsky equation has an exponential relationship between these two viscosities. Therefore, replacing just a small amount of the linear polymer can result in large reductions in viscosity. It should perhaps be pointed out that while our blend results are consistent, we have limited ourselves to blends containing only high molecular weight linear polymers. It is of interest to determine how molecular

weight of the linear polymer, particularly at a similar molecular weight as that of the hyperbranched polymer, would affect blend properties. In this regard, Uppuluri et al.[5] found linear PANAM polymers with the same molecular weight as its dendritic counterpart to exhibit higher viscosity, suggesting that blends of such components would exhibit rheology consistent with our results. However, more work is needed in this regard, and our current effort focuses on understanding this issue using a linear polymer with a range of molecular weights.

Conclusions

Hyperbranched polyesters in NMP solvent exhibited Newtonian behavior for different generations up to generation 5 and for concentrations as high as 50 wt %, indicating the absence of physical entanglements in these systems. The hyperbranched polymers also have much lower solution viscosities than linear polymers due to the lack of entanglements and their very low intrinsic viscosities. The solution viscosities depended only slightly on the generation number, with the smaller generations exhibiting lower viscosities. In addition, the hydrodynamic radius for hyperbranched polyesters scaled as $R_h \sim M^{0.39}$, indicating a less packed structure than dendrimers. The empirical Lyons−Tobolsky equation relating solution viscosity to intrinsic viscosity and concentration was a good fit for the hyperbranched polyester data up to 30 wt % concentration. All generations also had approximately the same apparent activation energy of flow within the temperature range studied.

Replacing linear polymers with hyperbranched polymers in blends resulted in drastic reductions in blend viscosities. Such reductions could be attributed to two factors. The first factor involved the interference of physical entanglements between linear polymers by the globular-shaped hyperbranched polymers. The second factor related to the concomitant decrease in the blend's intrinsic viscosity upon addition of hyperbranched polyesters.

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