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Rheology of Fractionated and Unfractionated Hyperbranched Polyesters

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Introduction

A class of branched polymers that has received increasing attention in recent years are hyperbranched polymers (HBPs). These are randomly branched polymers synthesized from a one-pot polycondensation of multifunctional AB_x ($x \geq 2$) type monomers where A reacts exclusively with B. Hyperbranched polymers exhibit many of the intriguing rheological properties of regular dendrimers; e.g., the intrinsic viscosity varies nonmonotonically with molecular weight,[1] but they are much cheaper to produce compared to dendrimers. This makes HBPs ideal candidates for applications such as coating agents and rheology modifiers.[2] However, one drawback of the one-pot synthesis method is that the HBPs produced have extremely high polydispersity which tends to smear out the desired dendrimer-like rheological properties. An obvious route to reducing polydispersity and hence recovering some of the dendrimer-like properties in HBP systems is fractionation. This provides a strong motivation for studying the rheology of fractionated HBPs which is the primary subject of this note.

There have been comparatively few rheological studies of low-polydispersity HBPs owing to the difficulty of obtaining such samples. Simon et al.[3] have studied the melt rheology of fractions obtained by preparative SEC of short chain branched PMMAs synthesized from a self-condensing vinyl polymerization process. Dorgan et al.[4] have studied the melt rheology of low-polydispersity, short chain branched polystyrenes prepared by anionic polymerization. However, while these studies have been valuable in discussing the qualitative rheological characteristics of these systems, attempts to model the rheology quantitatively were either absent[3] or unsuccessful[4] in these studies. In this note, we quantitatively model the rheology of fractionated short chain branched HBPs (i.e., short spacer length between branched points) using a dynamic scaling model for unentangled fractals that has previously been applied to unfractionated HBPs.[5,6] The excellent agreement we find between our dynamical scaling model and the melt rheology of fractionated and unfractionated HBPs in this and previous studies[5,6] conclusively shows that short chain branched HBPs are unentangled irrespective of molecular weight and polydispersity.

Theoretical and Experimental Details

Theory. To model the MWD for both the parent and the fractions, we use the two-parameter Schulz-Zimm (S−Z) distribution[7] for which the weight fraction is given by

Table 1. Molecular Weight Distribution Parameters

material	M_w	M_n	n	$1/\lambda$
P135	133 000	12 000	−0.3	133 500
F260	261 000	61 000	1.5	100 000
F100	95 500	24 000	1.0	45 500
F50	46 500	15 000	0.3	29 500
F10	12 000	8 000	2.7	2 500

Table 2. Glass Transition Temperature and Dynamic Rheology Fitting Parameters

material	T_g (°C)	ϵ_x (s^{-1})	G_0 ($\times 10^6$ Pa)
P135	47.7	9	1.8
F260	46.1	9	2.0
F100	43.4	17	2.2
F50	39.9	37	2.0
F10	45.6	45	2.5

$$W(M) = \frac{\lambda^{n+1}}{\Gamma(n+1)} M^n \exp(-\lambda M) \qquad (1)$$

where n and λ are parameters characterizing the distribution and $\Gamma(x)$ is the gamma function. For the HBP fractions, the use of eq 1 is purely phenomenological, while for unfractionated HBPs, the use of eq 1 can be justified from earlier studies[5,6] (recalling that $W(M) = n(M)M/M_0$ where $n(M)$ is the number density and M_0 is the monomer molecular weight).

To model the rheology, we use a dynamic scaling model based on the Rouse model which is described in detail in refs 5 and 6. Specifically, we use eqs 6 and 11 in ref 5 to model the rheology of fractionated and unfractionated HBPs, respectively (using $\tau = 1 - n$ and noting that $\Gamma(x,y) = \int_y^\infty t^{x-1} e^{-t}\, dt$ is the incomplete gamma function in these equations). To complete our specification of the rheology, we also need the fractal dimension d_f of HBP chains in the melt (see eq 7 in ref 5). For both unfractionated (i.e., polydisperse) and fractionated (i.e., to a first approximation monodisperse) HBP melts, we have previously shown[5,8] that $d_f = d$, where $d = 3$ is the spatial dimension. This arises from the fact that the HBP molecules exist in a quasi-c^* state, which also justifies the assumption that the HBP chains are unentangled.

Experiment. The AB_2 monomer used in our study is dimethyl 5-(4-hydroxyalkoxy)isophthalate. A detailed description of the synthesis of the parent HBP can be found in Keeney[9] and Feast et al.[10] The fractions were obtained from the parent polymer by precipitation in toluene on addition of methanol. A detailed description of the fractionation procedure can be found in De Luca.[11] The molecular weight distribution was characterized by triple detector size exclusion chromatography (Viscotek) in THF using a 90° laser light scattering detector (RALLS, $\lambda_0 = 670$ nm). The samples and their molecular weights are shown in Table 1. The parent polymer is abbreviated by the letter P followed by its molecular weight. The fractions are abbreviated by the letter F followed by their molecular weights. The glass transition temperature T_g of each sample was measured using DSC (Perkin-Elmer Pyris 7 using a heating rate of 10 °C/min), and measured values are collected in Table 2. Dynamic rheological spectra were obtained on a Rheo-

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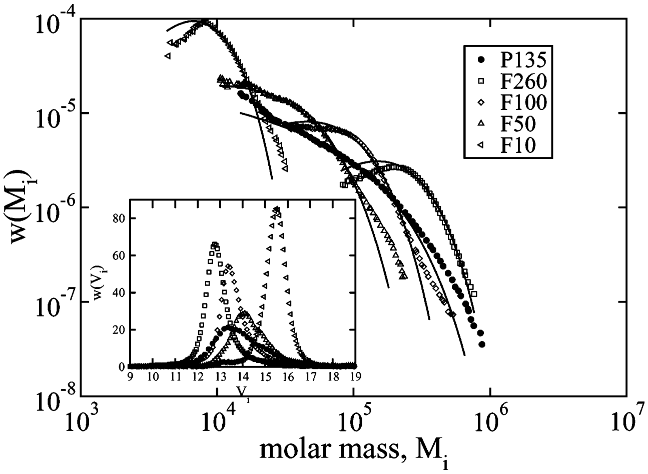

Figure 1. Weight fraction $W(M_i)$ of the parent polymer and fractions. Symbols are for the empirical data, and solid lines are least-squares fits using eq 1. Inset: $W(V_i)$ (weight fraction of elution volume V_i) of the parent polymer and fractions.

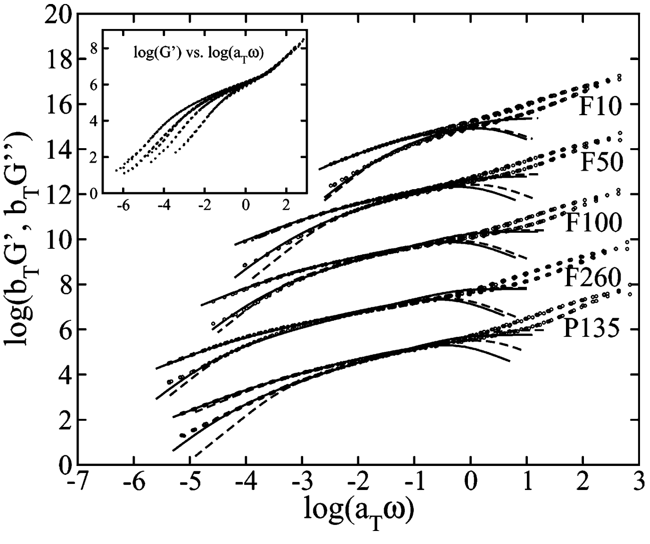

Figure 2. Master curves of dynamic moduli for all the samples. All data sets were vertically shifted arbitrarily for clarity and referenced to a temperature of $T_g + 20$ °C. The symbols represent the experimental data points, solid lines are fits using eq 11, and dashed lines are fits using eq 6 in ref 5. Inset shows that a reference temperature of $T_g + 20$ °C superposes the high-frequency data (G' in the case) reasonably well.

metrics ARES rheometer using a 10 mm diameter parallel plate geometry. Other details for SEC, DSC, and rheometry are essentially the same as those in ref 5.

Results and Discussion

Size Exclusion Chromatography. The weight-average molecular weight M_w and the weight fraction $W(M_i)$ are calculated using eqs 14 and 15 in ref 6, respectively, following the same procedures outlined in that reference.[12] Figure 1 (inset) shows the normalized RI detector response $W(V_i)$ against elution volume V_i for all the fractions and the parent HBP. Note that the mean molecular weights for the fractions are fairly evenly distributed throughout the MWD of the parent polymer so that the fractions are representative of the molecular weight range present in the parent HBP. Figure 1 also shows the weight fraction $W(M_i)$ for the parent HBP and the fractions. To minimize errors in the fitting, we have removed the high or low molecular weight tails of the experimental data where either the LS or RI signals are too low.[5] The plot also shows fits to the experimental MWD using the Schulz−Zimm distribution (eq 1), and the resultant fitting parameters n and λ are given in Table 1. We see that the Schulz−Zimm distribution captures the MWD of all samples reasonably well though it slightly underpredicts the high molecular weight tail of the distribution. This in turn leads to a slight underprediction of G' at the lowest frequencies in our rheological model (see next subsection). It would of course be possible to model the MWD more accurately by using a more sophisticated parametrization involving more fitting parameters. However, we note that the S−Z distribution is mathematically convenient for modeling the rheology, and the resultant discrepancy in the rheology between theory and experiment is very small. We have therefore chosen to retain the Schulz−Zimm parametrization for the MWD in this study.

Linear Rheology. In Figure 2 we show the results of the dynamic shear experiments for all our samples. The data for all our samples have been time−temperature shifted to a reference temperature of $T_g + 20$ °C, and this procedure approximately superposes the high-frequency part of the different samples (see inset of Figure 2). At the lowest frequencies we have been able to probe, none of our samples exhibit classical terminal scaling ($G' \propto \omega^2$ and $G'' \propto \omega$). Instead, the observed low-frequency scaling exponent for G'' varies from 0.92 to 0.96 and that for G' from 1.22 to 1.42, indicating the presence of slow relaxation modes in all our samples. (It was not possible to probe lower frequencies because this involved exposing our samples to elevated temperatures for long periods which led to sample degradation problems.) We note that nonterminal scaling was also observed in both the studies of Simon et al.[3] and Dorgan et al.,[4] indicating that the presence of slow modes is a generic feature in many HBP systems. At intermediate frequencies, the dynamic moduli show an apparent power law behavior (spanning about 2 decades in frequency for the highest molecular weight samples) analogous to that seen in near-critical gels and microgels. However, this power law behavior in the dynamic moduli is in fact only *apparent*, as we find that for all our samples tan δ is not constant in this regime.

In Figure 2 we show fits to the dynamic moduli using G_0 (the unrelaxed plateau modulus) and ϵ_x (the relaxation rate for the spacers) as our fitting parameters for two different assumptions for the MWD. In the first case, we assume that the sample is monodisperse with molecular weight equal to M_w (dashed line) while in the second case we account for the full molecular weight distribution, i.e., using the Schulz−Zimm parameters determined in the previous subsection (solid line). The fitting parameters G_0 and ϵ_x in the latter case are reported in Table 2. The magnitude and variation of these parameters are similar to what we have found in our previous studies on unfractionated HBPs,[5,6] and a detailed discussion of these issues can be found in these studies.

In this note, we wish to focus on the fact that we obtain excellent fits to all the rheological data (at low and intermediate frequency) when we explicitly account for the molecular weight distribution of the samples. (As already mentioned, the slight underprediction of G' at the lowest frequencies is presumably due to the slight underprediction of the high molecular weight tail by the S−Z distribution.) The monodisperse model, on the other hand, performs reasonably for samples with lower polydispersity (F10, F100, and F260) but performs poorly for the samples with higher polydispersity (P135, F50), especially for the low-frequency G' data. (The rheological response at high frequencies is not predicted well because relaxation modes with $\epsilon > \epsilon_x$ have been neglected in our model.) This demonstrates that rheology is rather sensitive to the molecular weight distribution and, in particular, that the slow modes observed in Figure 2 are due to the ultrahigh molecular weight species in the exponential tail of the molecular weight distribution. The excellent fits to both the parent polymer and the fractions also conclusively proves that short chain HBPs are unentangled independent of molecular weight and polydispersity.

The fact that HBPs are generally unentangled has important implications for the use of HBPs as rheology modifiers. HBPs when added in trace quantities to polyethylenes migrate to the surface[13,14] and can cause apparent wall slippage due to reduced entanglement density at the HBP−polymer interface. This leads to better processing properties for the bulk polymer.[15]

Conclusions

In this study, we have reported results for the rheology and MWD of a short chain hyperbranched polyester and its fractions. We have been able to quantitatively model the rheology of the parent polymer and fractions by using a dynamical scaling model based on the Rouse model which incorporates the Schulz−Zimm parametrization for the MWD of the polymers. The excellent fits to both the parent HBP and fractions implies that short chain branched HBPs are unentangled, independent of molecular weight or polydispersity. This is in good accord with previous theoretical studies[5,8] which indicate that both polydisperse and monodisperse short chain branched hyperbranched polymers exist in the quasi-c^* state where chains are only marginally overlapped and therefore unentangled. The general lack of entanglements in short chain branched HBPs may have important implications for their use as rheology modifiers.

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(12) One complication in the calculation of M_w was the fact that in the SEC traces of F100 and F10 we observed a small peak at low elution volumes (i.e., high molecular weights) due to a small amount of aggregation in THF. To correct for this artifact, we have removed this peak when integrating the LS signal to calculate M_w. The resultant values for M_w (reported in Table 1) are then in good agreement with those obtained previously by De Luca[11] using static light scattering in chloroform, which is a better solvent for our polymers compared to THF. (Unfortunately, it was not possible to repeat our SEC measurements in chloroform as the necessary equipment was not available for this study.)

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