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Rheological characteristics of hyperbranched polyesters

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Summary

When the effects of physical aging below T_g are erased, the rheological response of a series of aliphatic hyperbranched polyesters is Newtonian and the melt viscosity scales roughly linearly with M_w at high M_w, indicating entanglement to be absent. The rheological behavior is also highly sensitive to the nature of the terminal groups, suggesting the overall behavior to be close to that of an assembly of compact core-shell "particles". There are therefore strong parallels between the physical behavior of the hyperbranched polyesters in question and that of their ideal dendrimer analogues.

Introduction

Bulk rheological characterization of dendritic polymers is scarce in the literature [1-3]; dendrimers with well-defined architectures require multi-step synthesis [4-8], and obtaining sufficient quantities may be prohibitively expensive. Hyperbranched polymers (HBPs), on the other hand, based on one-pot or pseudo-one-pot condensations of AB_2 chain extenders with a poly B-functional core, can be much cheaper to produce [8-11], and their bulk rheological behavior is often of direct relevance to potential practical applications, e.g. coatings [12] and flow-enhancement or toughening of conventional polymers [13]. Unlike perfect dendrimers, HBPs display irregular, partially branched structures, significant polydispersity and chemical inhomogeneity. This may need to be considered when interpreting rheological data, accurate measurements of the molar mass distribution (MWD) being particularly important. Some authors nevertheless continue to use a single dendrimer-equivalent number average molar mass, M_n^{deq}, which cannot provide a full description of a polydisperse HBP. M_n^{deq} is derived by assuming all chain extenders originally present in the reaction mixture to be attached a core molecule and hence the absence of cyclics, residual monomer and products from side reactions [14]. As well as being of practical relevance, the scaling of quantities such as the viscosity, η, reflects the extent to which the physical properties of HBPs are comparable with those of perfect dendrimers, and hence the extent to which they may provide a low cost alternative to dendrimers. Available accounts of the bulk rheological properties of dendrimers suggest an assembly of compact particles (the “ball bearing” effect [8]) rather than the conventional picture of an entangled melt evoked for high molecular weight linear polymers [1-3]. Interactions between the surfaces defined by the dendrimer conformations, and hence the chemical nature of the groups present at these surfaces, are therefore likely to be of considerable importance [8, 15, 16]. Indeed, manipulation of the surface chemistry provides a powerful means of tailoring the rheological properties without altering the dendritic architecture. In what follows we examine whether this behavior is reflected by that of polyester HBPs with a range of molar masses, M. Since a key to meaningful interpretation is adequate characterization of the MWD, this aspect of the work is discussed in some detail.

Experimental

The HBPs (Perstorp Chemicals) are prepared by a one-pot polycondensation of 2,2 *bis*-hydroxymethyl propionic acid (*bis*-MPA) with a tetrafunctional ethoxylated pentaerythritol core. Each grade is designated by a pseudo-generation number by analogy with the perfect dendrimer, such that the n^{th} pseudo-generation corresponds to a reaction mixture containing

$$4\sum_{i=0}^{n-1}2^{i} \qquad \textbf{(1)}$$

bis-MPA molecules for every core molecule [10]. All materials were carefully dried and stored under vacuum prior to use. GPC was carried out with a Waters 150CV, modified for on-line differential viscosimetry, using the universal calibration method [17]. Measurements were made in N,N-dimethyl formamide (DMF) at 60 °C with TSK-Gel Alpha columns, specifically designed for polar solvents. Further technical details are given elsewhere [18]. For rheological characterization, use was made of a Rheometrics RDA II rotational rheometer with 25 mm and 50 mm diameter parallel plates, and the measurements checked using the cone and plate geometry (50 mm diameter, 0.02 and 0.04 rad incline). Comparison of data obtained under dynamic and steady state conditions (shear rates from 0.01 to 1 s^{-1}) showed the Cox-Merz rule [19] to be valid for the dried HBPs for dynamic strain amplitudes up to at least 10%, and over the full range of temperatures investigated. Therefore, no distinction is made between the steady state viscosity and the complex viscosity. Glass transition temperatures (strictly speaking, α transition temperatures), T_g, were taken to correspond to the observed maximum in loss modulus in cooling scans at 5 K min^{-1} in dry N_2 with a measurement frequency of 6.28 rad s^{-1}. Calorimetric data were obtained by differential scanning calorimetry (DSC, Perkin Elmer DSC 7). Fourier transform infrared spectroscopy (FTIR, Nicolet Magna-IR 560) was carried out in attenuated total reflectance mode (ATR, Golden Gate).

Results and Discussion

Although non-linear molecules may show different scaling of the hydrodynamic volume, V_h, with M to linear standards, universal calibration is known to give accurate results for certain dendritic polymers [9, 20]. With functional molecules, characterization is often made difficult by aggregation and/or specific interactions with the stationary phase in the column. However, results for the present HBPs end-capped with relatively non-polar trimethylsilane ($-OSiMe_3$) were consistent with results for the as-received -OH terminated HBPs. Moreover, hydrolysis of the end-capped HBPs to restore the -OH groups gave identical results to those obtained before end-capping. Figure 1(a) gives results for a 3 pseudo-generation HBP re-precipitated from methanol to remove low M material and facilitate unambiguous determination of M_n. Absolute changes in MWD inferred from the GPC traces agreed well with those predicted from the degree of conversion of the -OH groups (from ^{1}H-NMR [18]) and the MWD of the unmodified HBP. This is illustrated in Table I, in which measured values of M_n and M_w are compared with

$$M_n = M_{no}\left(1+\frac{\delta M_s}{M_{no}}\right);\quad M_w = M_{wo}\left(1+\frac{\delta M_s}{M_{no}}\right) \qquad \mathbf{(2)}$$

where M_{no} and M_{wo} are the number and weight average molar masses of the unmodified HBP respectively, $M_s = 72.19$ g mol^{-1} is the increment in M associated with replacement of -OH by -OSiMe$_3$ and δ is the mean number of -OSiMe$_3$ groups per molecule estimated from M_{no} and the overall degree of conversion.

Table 1. Comparison of measured and calculated molar mass averages for different degrees of trimethylsilylation of a 3 pseudo-generation HBP.

Degree of end-capping	Measured M_n [g mol^{-1}]	Calculated M_n [g mol^{-1}]	Measured M_w [g mol^{-1}]	Calculated M_w [g mol^{-1}]
0.00	3510	3510	7140	7140
0.21	4280	3995	8120	8127
0.48	5140	4619	9350	9396
0.71	5560	5150	9970	10476
0.94	6570	5681	11800	11557

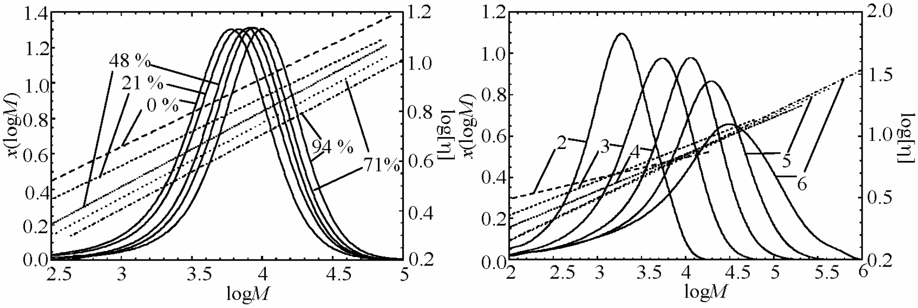

Figure 1. (a) GPC results for the MWD (solid curves) and [η] (hatched curves) for precipitated 3 pseudo-generation HBP with the degrees of conversion of -OH to trimethylsilane as indicated; (b) GPC results for as-received HBPs with the pseudo-generation numbers indicated

Table 2 gives data for the as-received HBPs used for the rheological measurements, and Figure 1(b) gives the corresponding GPC traces. Since these specimens were not re-precipitated, M_n for the 3 pseudo-generation HBP was lower than that in Table 1. M_n^{deq} for the different grades are also given in Table 2, suggesting them to overestimate M_n, particularly for the highest pseudo-generation numbers. Moreover, there was considerable uncertainty in M_n for the as-received HBPs owing to its sensitivity to the limits of integration used to calculate it from the GPC data [21]. This is illustrated in Table 2, where values calculated by setting the lower integration limit to just above M for the un-reacted core molecules are given along with values (in brackets) calculated using a much lower integration limit, for which the experimental error was large. Although the former are retained in the subsequent discussion, the presence of impurities cannot be ruled out; even lower M_n (by about 30 %) have been obtained in similar materials by vapor pressure osmometry [14]. Since this implies uncertainty in the polydispersity given by M_w/M_n, a polydispersity exponent, τ, was estimated from $M_z \sim M_w^{(3-\tau)}$ [20]. τ was almost constant and equal to 2.2 over the whole data range, consistent with percolation-type structure build-up [22, 23].

Table 2. GPC-viscometry results for the HBPs in DMF. In the evaluation of M_n, M below 300 g mol^{-1} were excluded from the calculations owing to uncertainties associated with the low M tail of the MWD. Values calculated with an integration limit of 100 g mol^{-1} are given in brackets for comparison.

	Pseudo-generation number				
	2	3	4	5	6
M_n^{deq} [g mol^{-1}]	1750	3608	7323	14753	29614
M_p [g mol^{-1}]	1950	5640	10630	18480	31410
M_n [g mol^{-1}]	1130 (890)	2520 (2090)	4340 (2710)	5880 (3180)	5020 (2970)
M_v [g mol^{-1}]	1850	5360	10120	17460	41260
M_w [g mol^{-1}]	2400	7310	13690	26020	55510
M_z [g mol^{-1}]	4130	14340	29150	69480	200220
M_w/M_n	2.12 (2.55)	2.89 (3.35)	3.15 (4.87)	4.43 (7.81)	11.0 (18.0)
$[\eta]$ [ml g^{-1}]	4.96	5.85	6.99	7.96	10.03
Log K	0.0388	-0.2323	-0.4812	-0.5414	-0.6372
a	0.201	0.268	0.331	0.340	0.355

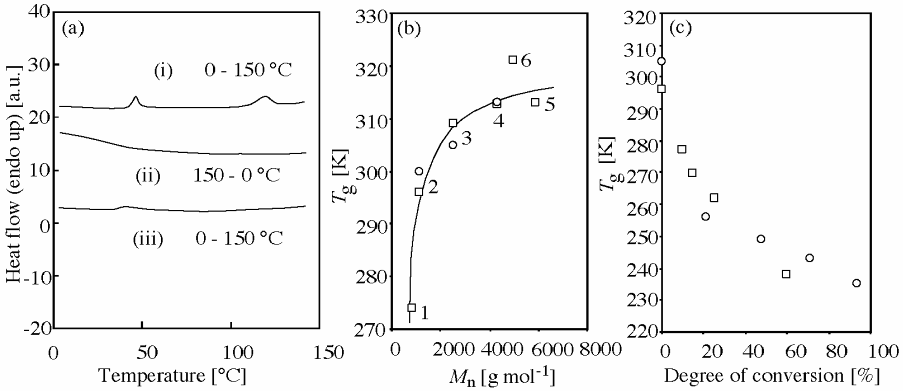

Figure 2. (a) DSC curves for a 4 pseudo-generation HBP on successive heating and cooling at 10 Kmin^{-1}; (b) comparison of T_g for HBPs with different M_n and functionality (circles - DSC heating scans at 10 K min^{-1}; squares - rheological measurements; the pseudo-generation number is indicated in each case and the solid curve is a fit of Equation 4 to the data); (c) the effect of different degrees of conversion of -OH terminal to $-OSi(CH_3)_3$ (circles) and $-O_2C(CH_2)_{10}CH_3$ (squares) for the 3 and 2 pseudo-generation HBPs respectively.

All the HBPs investigated in the present work followed the Mark-Houwink law,

$$[\eta] = KM^{a} \qquad (3)$$

as shown in Figure 1. The Mark-Houwink exponents, a (Table 2), were relatively low, but increased somewhat with pseudo-generation number. It is inferred that $V_h \sim M[\eta] \sim M^{1.2}$ to $M^{1.35}$ as opposed to $V_h \sim M^{1.5}$ to $M^{1.7}$ observed for linear polymers (depending on the solvent quality). For comparison, macroscopic measurements in *N*-methyl pyrrolidine (NMP) using an Ubbehlode capillary viscometer at 25 °C, taking $M = M_v$, gave $a \sim 0.2$, implying $V_h \sim M^{1.2}$. Molecular dynamics simulations (Cerius^2, MSI) of isolated perfect dendrimer analogues at 400 K also suggest a power law dependence of the radius of gyration, $R_g \sim M^{0.34}$ [24], so that $V_h \sim M^{1.02}$, assuming the hydrodynamic radius to be proportional to R_g. This implies nearly ideal space-filling conformations, that is, a near constant number of segments per unit volume. In the HBPs, ^{13}C NMR indicates degrees of branching of the order of 40 to 50 % [24, 25] according to the definition of Hawker *et al.* [26], so that less compact configurations and hence stronger scaling than for the ideal dendrimer are expected

The glass transition in the -OH terminated HBPs depends strongly on their thermal history. A melting-like glass transition was observed in DSC heating scans of specimens that had undergone physical aging below T_g, including the as-received HBP stored at room temperature. As well as the enthalpic peak associated with T_g, a second peak was observed at about 120 °C in DSC heating scans of physically aged specimens (Figure 2(a)). This was associated with a densification of about 3 %, and some evidence from wide angle X-ray scattering for local ordering. On cooling from above 150 °C, the second peak disappeared and the glass transition was ill-defined. DSC data given in Figures 3(b) and 3(c) were therefore determined from heating scans at 10 Kmin^{-1} immediately after cooling from 150 °C to room temperature, rather than directly from cooling scans. Prior heating to 150 °C also made it easier to dissolve the specimens, particularly if they were immediately mixed with warm solvent without cooling to room temperature It is thought that the physical aging of the HBPs primarily involves the development of the hydrogen-bonded network, as reflected by changes in the -OH peaks in IR absorption spectra (Figure 3). That these interactions are of importance for T_g is borne out by Figure 2(c) where DSC results for different degrees of end-capping with trimethylsilane and a fatty acid are given. A similar fall-off in T_g with degree of conversion was observed in each case. T_g nevertheless increased with pseudo-generation number in the unmodified HBPs, in spite of an expected decrease in the ratio of the number of -OH groups to M of about 10 % as the generation number increases from 1 to 6, its changing very little beyond generation 3. Bearing in mind the uncertainty in M_n and the apparent scatter in T_g, as shown in Figure 2(b), the behavior was consistent with that generally observed for linear polymers at intermediate and high M_n;

$$T_g = T_{g\infty} - \frac{k}{M_n} \tag{4}$$

k is often associated with excess free volume at the chain ends [27], in which case for branched polymers it should be proportional to the number of chain ends per molecule [2], implying k/M_n to tend to a non-zero limit as $M_n \to \infty$ in the HBPs investigated here. However, any such interpretation implies a homologous series, whereas in these HBPs not only the end groups but also the relatively flexible core may have a strong influence on T_g. Indeed, expressing T_g as the sum of two limiting values of T_g weighted by the mass fractions of the core and the chain extenders respectively leads to an expression with the same form as Equation (4). For comparison, estimates from group contribution theory [28] for linear (*bis*-MPA)$_n$, that is, a linear polymer with the same ratio of –OH groups to M as in the HBPs in the high pseudo-generation number limit, gave $T_{g\infty}$ = 337 K, whereas the T_g of the un-reacted core was 218 K (DSC), implying the core/chain extender ratio to be a significant, if not the most significant contribution to the observed variation in T_g with M_n.

It was also necessary to heat the specimens to 150 °C prior to measurements at lower temperatures in order to obtain reproducible rheological data. The importance of this precaution is shown in Figure 4, where the evolution of the viscoelastic functions as a function of frequency is given for the 5 pseudo-generation HBP. The as-received HBP showed a relatively high η and non-Newtonian behavior (η decreased roughly as $\omega^{-0.55}$), whereas the same HBP heated to 150 °C prior to the measurements was Newtonian. The rheological response of the as-received HBP was also characterized by a plateau in the storage modulus G' vs. T above T_g at low frequencies, that is, solid-like behavior, indicating formation of a physical network. This behavior was recovered in HBPs heated to above 150 °C after a few days' physical aging below T_g, demonstrating break-up of the network to be reversible and hence not to be a result of degradation, which is insignificant in this temperature range. This behavior was again attributed to hydrogen bonding, and it disappeared at high degrees of end capping, for which little hydrogen bonding was expected.

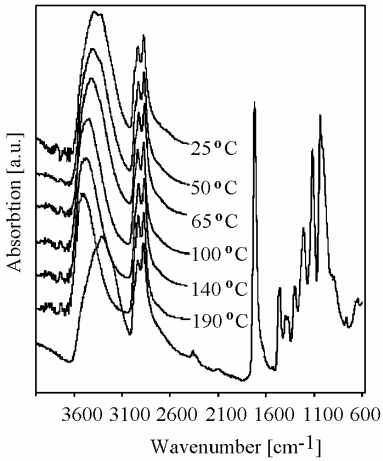

Figure 3. ATR-FTIR: full spectrum for as-received 2 pseudo-generation HBP and spectra taken during stepwise cooling from 190 °C to the temperatures indicated. The shift in the –OH peak at about 3300 cm^{-1} reflects a decrease in hydrogen bonding.

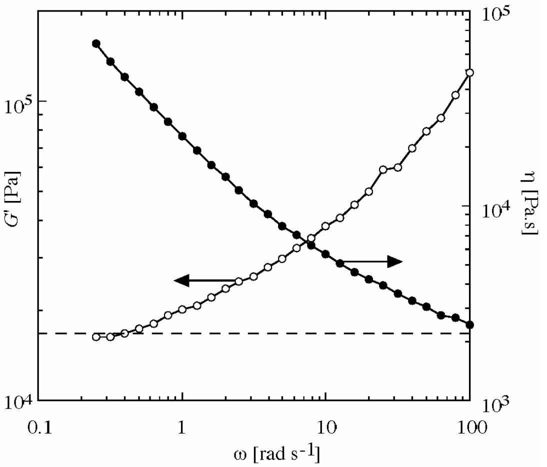

Figure 4. Rheological behavior at 100 °C of a 5 pseudo-generation HBP heated directly from room temperature to the test temperature; the hatched horizontal line indicates the viscosity measured immediately after cooling from 150 °C (dynamic strain amplitude 10 %).

Figure 5(a) shows η as a function of M_w at three different temperatures above T_g in specimens heated to 150 °C prior to the measurements. At intermediate and high M_w, Rouse-like scaling, that is, $\eta \sim M$ was observed. The scaling was stronger at lower M_w, although the distinct chemical nature of the core and the chain extenders may be important in this regime, as suggested for T_g. η is shown as a function of temperature in Figure 5(b), indicating Arrhenius behavior, the activation energy increasing with M_w, consistent with previous results [25]. Finally, Figure 5(c) shows the dependence of η on the degree of end-capping, with the expected strong decrease in η as the conversion of the –OH groups increased. Rouse-like behavior implies an absence of melt entanglement coupling. However, it is not *a priori* clear whether this is due to the compact conformations inferred from the solution behavior, or whether it is because M_w is less than the critical molar mass, M_c. A first step to answering this question was to estimate the entanglement molar mass M_e of a linear analogue to the dendritic structure in question. As for T_g, (*bis*-MPA)$_n$ provided the reference, and the group contribution method [28] gave $M_e \approx$ 10'000 g mol^{-1} and $M_c \approx 2M_e \approx$ 20'000 g mol^{-1}. Since strong scaling of η with M characteristic of an entangled melt should only be apparent for $M_w > M_c$, if the above estimate of M_e is reasonable, pseudo-generations 2 to 4 ought not show entanglement effects, regardless of their degree of branching. The behavior of the higher pseudo-generation numbers, on the other hand, does indicate that the entanglement threshold for the HBPs, if it exists, should be very much higher than M_e in its linear counterpart.

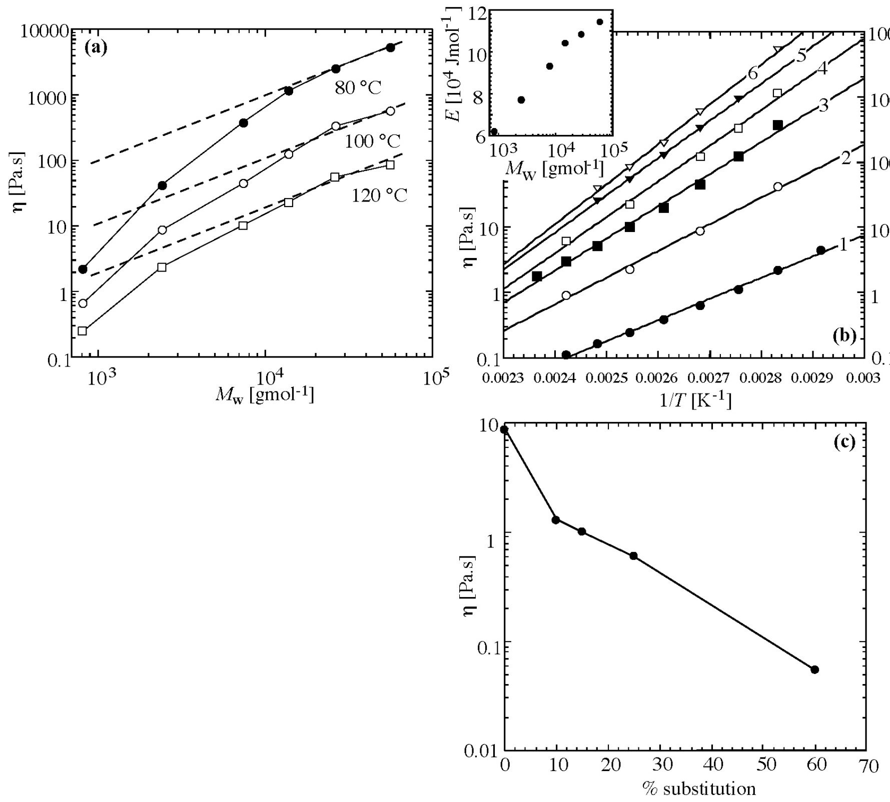

Figure 5. (a) η as a function of M_w at three different temperatures above T_g; (b) η as a function of T for different M_w (inset, Arrhenius activation energy as a function of M_w); **(c)** η in the 2 pseudo-generation HBP at different levels of end-capping with -$O_2C(CH_2)_{10}CH_3$.

Conclusions

Provided suitable precautions are taken to erase the effects of physical aging below T_g, the rheological behavior of a series of aliphatic hyperbranched polyesters is found to be Newtonian, with a melt viscosity that scales roughly linearly with M_w at high M_w, indicating entanglement effects to be absent. The rheological response is also found to be highly sensitive to the nature of the terminal groups, suggesting the overall behavior to correspond closely to that of an assembly of compact core-shell "particles" whose interactions are essentially surface-surface interactions via the shell, which is assumed to contain the functional groups. Although this ideal picture does not take into account back-folding and incomplete branching, for example, it is inferred that the HBPs show similar physical behavior to that of their ideal dendrimer analogues in this respect.

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