5792 *Macromolecules* **2001,** *34,* 5792−5798

Synthesis, Structure, and Properties of Core-Terminated Hyperbranched Polyesters Based on Dimethyl 5-(2-Hydroxyethoxy)isophthalate

David Parker and W. James Feast*

Interdisciplinary Research Centre in Polymer Science and Technology, University of Durham, Durham DH1 3LE, UK

Received March 23, 2001; Revised Manuscript Received June 5, 2001

ABSTRACT: The molecular weight of hyperbranched polyesters, prepared by condensation polymerization of the AB_2 monomer dimethyl 5-(2-hydroxyethoxy)isophthalate in the presence of either a B_3 core (trimethyl 1,3,5-benzenetricarboxylate) or a B_2 core (dimethyl isophthalate), was controlled by varying the core-to-monomer ratio. During polymerization polycondensation, cyclization and core-termination reactions occurred in competition. The polyester's weight-average molecular weight continued to increase even after complete consumption of the A groups by cyclization and core termination, which is postulated to result from a redistribution of polymer chains by ester−ester interchange reactions. The polymers are soluble in common organic solvents, and solutions have characteristically low intrinsic viscosities. The physical characterization of these polymers is reported.

Introduction

The investigation of polymers with highly branched topologies, in particular dendritic macromolecules, has become an important theme in polymer science. Dendritic macromolecules include well-defined regular monodisperse structures such as dendrimers plus the ill-defined polydisperse systems with varying degrees of branching that have been termed hyperbranched polymers. The latter have recently been defined as polymers that are based upon AB_m or latent AB_m-type monomers and which have a branch-on-branch structure and a maximum of one closed cycle per macromolecule.[1] Due to the inherent constraint that in AB_m-type systems each branched macromolecule can only contain a single A group, very high branching densities are possible without network formation.[2] At present, the majority of hyperbranched polymers are made by batch polycondensation of AB_m monomers. Flory, in a statistical analysis of AB_m polycondensation reactions, demonstrated that these are expected to yield polymers with very broad molecular weight distributions.[3] This conclusion was later reinforced by Müller and co-workers, who used a kinetic approach to show that the polydispersity index, x_w/x_n, where x_w and x_n are the weight-average and number-average degree of polymerization, respectively, of AB_2 hyperbranched polymers to be approximately $x_n/2$ at high conversion.[4] Broad distributions have a marked influence upon the solution properties of branched macromolecules,[2b] and various strategies have been employed to control the polydispersity of hyperbranched systems.

The molecular weight distribution can be controlled, to some extent, by copolymerization of AB_m monomers with core-forming molecules. In this approach the growing hyperbranched molecule is coupled with a multifunctional molecule, of B_f type, analogous to the central core of a dendrimer (Figure 1). The reaction of a core molecule with the single A (or focal) group of a hyperbranched molecule terminates growth from the focal group; hence, this class of polymer will be referred to herein as core-terminated hyperbranched polymers.

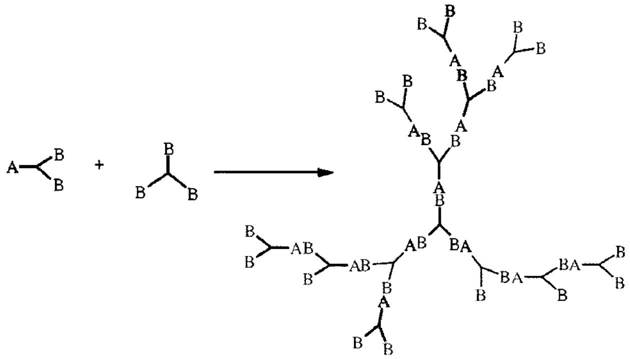

Figure 1. An idealized AB_2/B_3 core-terminated hyperbranched polymer.

Feast and Stainton reported an early example of the synthesis of a core-terminated hyperbranched polymer, by a batch process, in the melt polymerization of dimethyl 5-(2-hydroxyethoxy)isophthalate in the presence of trimethyl 1,3,5-benzenetricarboxylate (a B_3 core).[5] Control over the molecular weight and polydispersity of the resulting polymers was achieved by varying the core-to-monomer ratio. Molecular weight control has also been observed in the synthesis of core-terminated hyperbranched polycarbosilanes[6] and polyamidoamines.[7] In a related approach, Hult and co-workers synthesized aliphatic polyesters with relatively low polydispersities by the repeated addition of stoichiometric amounts of monomer to a core molecule in a synthesis designed to mimic the generations of a dendrimer.[8] The results of these early experiments are supported by theoretical kinetic analyses that predict the polydispersity of a core-terminated hyperbranched polymer, formed by the batch copolymerization of AB_m/B_f systems, to be both relatively low and dependent upon the core functionality.[9] Theoretical studies and computer simulations of the slow addition of AB_m monomers to a core under dilute conditions have been used to predict that control may be achieved over the molecular weight, polydispersity, and degree of branching of hyperbranched polymers using this method.[10] The

10.1021/ma010502c CCC: \$20.00

technique has been demonstrated experimentally in the synthesis of hyperbranched polyglycerols,[11] poly(phenylacetylene),[12] and poly(siloxysilane).[13]

Although theoretical treatments of hyperbranched polymerizations are often simplified by neglecting the possibility of intramolecular cyclization reactions,[9b] there is an increasing body of evidence demonstrating that this is not always a realistic assumption.[14] Cyclization is thus expected to compete with both core termination and polycondensation, and this has been observed in the synthesis of a number of core-terminated hyperbranched polymers.[11,13,14b,15]

We recently described the melt polymerization of dimethyl 5-(2-hydroxyethoxy)isophthalate in detail, and we report here the effect of introducing core molecules into the polymerization.[14e]

Experimental Section

All reagents were purchased from either Fluka or Aldrich Chemicals and used as received without further purification.

Instrumentation. Mass spectra were recorded on a Kratos MALDI IV instrument, using 2,5-dihydroxybenzoic acid as the matrix and collecting data over 200 laser shots in linear mode with laser powers typically in the region of 125 (ca. 15% transmission). Molecular weight distributions were obtained by size exclusion chromatography using both chloroform and tetrahydrofuran as solvent. SEC in chloroform utilized three 5 μm columns of PLgel with pore size 100, 10^3, and 10^5 Å, calibrated against polystyrene standards and used an ERC 7515A refractive index detector. SEC in THF employed PL gel columns (3 × 300 mm, polystyrene divinylbenzene copolymer beads, mixed pore sizes) maintained at 30 °C. A Viscotek differential refractometer, viscometer detector, right-angle laser light scattering (RALLS) detector, and data capture unit (DM 400) were used in conjunction with TriSEC GPC software (version 3.0). Dilute solution viscometry measurements were made with a Schott-Gerate automated viscometer system utilizing a Schotte-Gerate Ubbelohde viscometer tube (bore size 0.46 mm), immersed in a constant temperature water bath at 25 °C. Differential scanning calorimetry (DSC) measurements were recorded using either a Perkin-Elmer DSC 7 or a Perkin-Elmer Pyris 1. The polymer samples were annealed at 250 °C and cooled at a rate of 50 °C $\min^{-1}$ to 30 °C. DSC measurements were made over a temperature range of 30−250 °C using a heating rate of 10 °C $\min^{-1}$. The value for the glass temperature was taken as the temperature at the midpoint of the observed ΔC_p.

Monomer Synthesis. Dimethyl 5-(2-hydroxyethoxy)isophthalate was synthesized using the method reported previously.[14e]

Representative Polymerization Procedure. Dimethyl 5-(2-hydroxyethoxy)isophthalate (4.83 g, 19.06 mmol), dimethyl isophthalate (0.172 g, 0.89 mmol), $Mn(OAc)_2$ (3.8 mg, 0.021 mmol), Sb_2O_3 (3.2 mg, 0.011 mmol), and $(PhO)_3PO$ (2.0 mg, 0.006 mmol) were heated at a rate of 10 °C/min to 240 °C and held at that temperature for a period of 24 h. The polymerization was carried out under a constant nitrogen flow and stirred at a rate of 125 rpm. After cooling, the polymer was obtained as a brittle glass (3.9 g). No purification of the polymer was carried out at this stage.

Results and Discussion

A series of core-terminated hyperbranched polyesters have been prepared by melt condensation copolymerization of the AB_2 monomer dimethyl 5-(2-hydroxyethoxy) isophthalate with various core molecules. The synthesis of the monomer from 5-hydroxyisophthalic acid was accomplished using the route reported previously.[14e] Copolymerization of the AB_2 monomer and core was carried out in the melt at 240 °C in the presence of a transesterification catalyst, and a stream of nitrogen gas was employed to remove the methanol condensate. A series of polymers were produced in this way by varying the type of core and the core-to-monomer ratio. Two cores of differing functionality were investigated, namely dimethyl isophthalate (a B_2 core) and trimethyl 1,3,5-benzenetricarboxylate (a B_3 core). Attempts to copolymerize a monofunctional core (B_1) using either methyl benzoate or methyl 4-*tert*-butylbenzoate were unsuccessful as these were too volatile at the polymerization temperature. The resulting polymers were obtained as brittle glasses that had a pale yellow to straw brown coloration. These were readily soluble in chloroform, and samples reprecipitated from methanol were obtained as free-flowing white powders. Only as-made samples were analyzed in this report to avoid any effects of partial fractionation during reprecipitation.

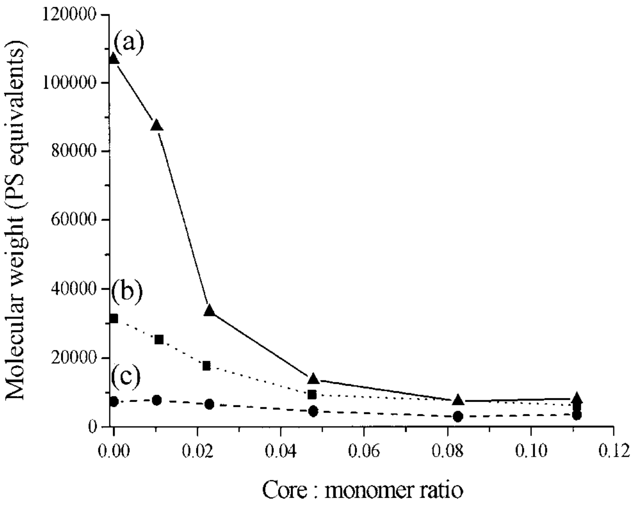

Figure 2. Molecular weights (polystyrene equivalents) of core-terminated hyperbranched polyesters, as determined by SEC in chloroform, vs core:monomer ratio. (a) M_w after 24 h polymerization, (b) M_w after 5 h polymerization,[5] and (c) M_n after 24 h polymerization.

Molecular Weight Distribution. The molecular weights of the hyperbranched polyesters were determined by size exclusion chromatography (SEC) using a triple-detection system employing a combination of differential refractometry, differential viscometry, and right -angle laser light scattering (RI-DV-RALLS). The SEC chromatograms revealed that the core-terminated hyperbranched polymers had broad molecular weight distributions typical of AB_2 condensation polymers.[14e] The molecular weights obtained by universal calibration were in good agreement with those obtained from the light scattering detector but appreciably higher than those derived from a conventional polystyrene calibration. Conventional polystyrene calibrations give a poor indication of molecular weight for these systems, but polystyrene equivalent molecular weights are reported here in order to compare these data with that presented in a previous study; see Figure 2.[5]

The ratio of core to monomer, used in the reaction, had a marked effect upon the eventual molecular weight of the hyperbranched polyesters. As the core content was increased, the molecular weight decreased rapidly, which is in good agreement with the reported behavior of both core-terminated polyesters[5] and polyglycerols.[11] The observed reduction in the molecular weight is associated with very low levels of core molecules, for example, increasing the B_3 core content from 1 to 2 mol

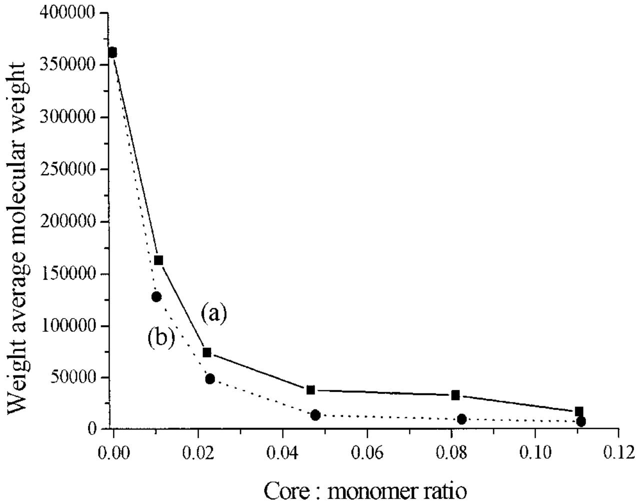

Figure 3. Effect of varying the core functionality upon the molecular weight (as obtained by SEC in THF using universal calibration) of core-terminated hyperbranched polyesters. (a) B_2 core; (b) B_3 core.

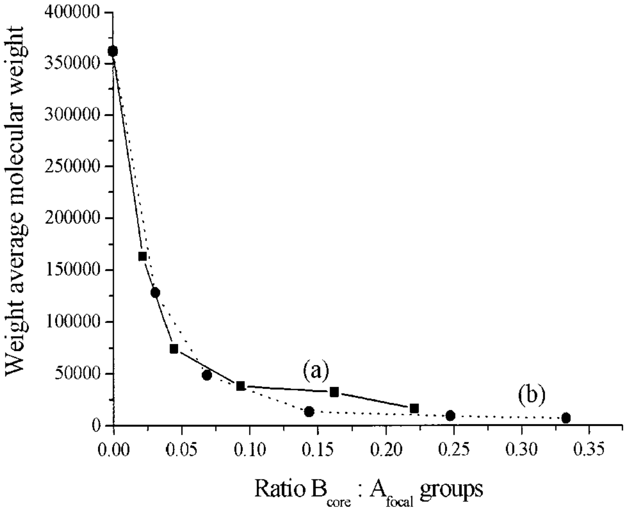

Figure 4. Effect upon the molecular weight weight of core-terminated hyperbranched polyesters (as obtained by SEC in THF using universal calibration) of varying the B_{core} group concentration. (a) B_2 core; (b) B_3 core

% reduced M_w (quoted as polystyrene equivalent molecular weights) by a factor of 2. Although the trend in molecular weight was similar to that observed by Feast and Stainton, for core-terminated polyesters after 5 h polymerization, longer polymerization times (24 h) gave markedly higher molecular weights. This implies that either complete consumption of the A groups has not occurred after 5 h polymerization or further polymerization proceeds via an alternative mechanism, such as ester–ester interchange.

Theoretically the use of a simple B_1 core could lower the molecular weight of a core-terminated hyperbranched polymer, and such monofunctional cores have been successfully employed in the synthesis of hyperbranched polyglycerols.[11] Hence, it is of some interest to know whether multifunctional cores react at more than one B group or whether they simply act as B_1 core terminators. The use of different core molecules allowed the effects of varying the core functionality to be investigated. Plots of molecular weight against core: monomer ratio, for the B_2 and B_3 core systems, show that the B_3 core has a greater influence on the final molecular weight than the corresponding B_2 core (Figure 3). The B_3 system has more core B groups available to undergo condensation reactions, and when the molecular weight is examined as a function of the ratio of core B groups to monomer A groups, as shown in Figure 4, there is little difference between the two core systems. Thus, it appears that the greater lowering of the molecular weight by the B_3 core is partly a consequence of the greater number of core B groups present. This also implies that more than one B group per core molecule can undergo a condensation reaction; otherwise, altering the core functionality would be expected to have no observable effect upon the resulting molecular weight.

The effect of a core molecule upon molecular weight is undoubtedly complex and the sum of at least two different processes. First, core molecules may act as chain terminators by consumption of unreacted A groups. Second, multifunctional core molecules may act as chain extenders if two or more of the functional groups are used. Theoretically, for a given core-to-monomer ratio, assuming 100% core termination and that all core B functionalities are used, the average molecular weight is independent of core functionality. For example, a B_3 core-terminated structure will have, on average, the same number of incorporated monomer units as its B_2 analogue but distributed among three arms or hyperbranched wedges rather than two. Hence, the observed effect of the different core systems upon the molecular weight of the hyperbranched polyesters is unexpected. This unexpected effect can be explained if we take into account the fact that the polymers reported in this work are not fully core-terminated and are in fact mixtures of macromolecules derived from either simple AB_2 polycondensation, ultimately terminated by cyclization, or core-terminated species (as described in a later section). The samples with low core B group content have lower levels of core-terminated species and higher amounts of macromolecules arising from simple AB_2 condensations. Simple AB_2 polycondensation tends to give higher molecular weights than AB_2/B_f core-terminated polymerizations, as shown in Figures 2–4, and hence the B_2 core-terminated systems, reported here, have higher average molecular weights arising from their greater content of non-core-terminated species.

Although incorporation of a core molecule imparts some degree of control over the final molecular weight of the hyperbranched polyester, there remains the question of whether any control can be achieved over the polydispersity. On first inspection there is an apparent lowering of the polydispersity, by copolymerization with a core molecule; however, this may simply be a consequence of the lower molecular weights attained in the core-terminated systems. To examine this phenomenon more fully, the polydispersities of the core-terminated polymers need to be compared to the polydispersities of the analogous AB_2 polymers of the *same molecular weight*. Such a comparison, as shown in Figure 5, reveals that there is no discernible difference between the polydispersities obtained for the simple hyperbranched and core-terminated hyperbranched polymers of a given molecular weight. We have previously postulated that these hyperbranched polyester systems undergo ester–ester exchange reactions, which may account for the loss of any control over polydispersity gained by the introduction of a core molecule.[14e]

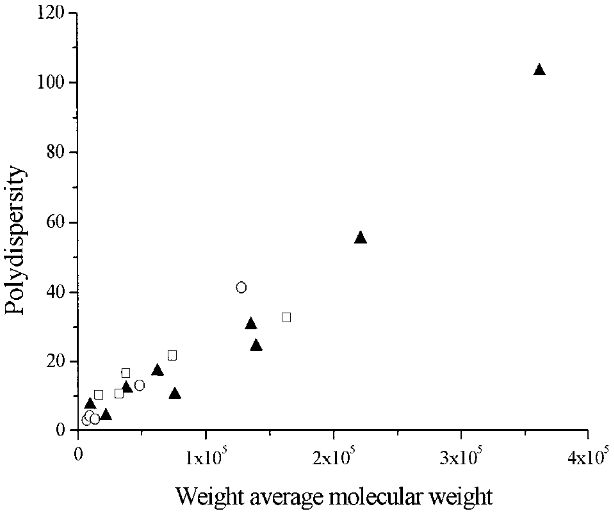

Figure 5. Comparison of the polydispersity of core-terminated and simple hyperbranched polyesters of varying molecular weight (squares denote a B_2 core, circles a B_3 core and triangles no core).

Level of Core Incorporation and Cyclization. The incorporation of a core molecule into a hyperbranched macromolecule prevents further growth from its single A group or focal point. Another potential growth limiting process is cyclization, which has been observed in the analogous AB_2 polymers.[14b,e] At the point of complete core termination, or cyclization, the polymer can no longer grow via a polycondensation mechanism, although the hyperbranched polymer derived from dimethyl 5-(2-hydroxyethoxy)isophthalate, without a core, continues to grow by a mechanism which is thought to involve ester−ester exchange. The relative amounts of core-terminated and cyclized oligomers were determined by matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS), and a typical spectrum is shown in Figure 6. As seen for other hyperbranched polymers, the high molecular weight region of the spectrum is typically under represented. Furthermore, the peaks corresponding to a degree of polymerization (DP) of greater than 8 are not fully resolved; hence, the analysis of the MALDI-TOF spectra was restricted to the region associated with DP 4−8 (m/z 800−2000). Individual species in the MALDI-TOF spectrum were observed as the parent species plus an attached cation $[M + Na]^+$. The mass of a particular oligomer may be calculated by a consideration of the polymerization process. An oligomer derived from n AB_2 units is the result of $(n - 1)$ condensation steps, and each successive condensation is accompanied by the loss of a single methanol moiety. Hence, the mass of an oligomer of n units is [(monomer mass) × (n) − (mass of methanol) × (n − 1)]. The occurrence of cyclization by intramolecular condensation results in the loss of an additional single methanol moiety, giving rise to peaks in the MALDI spectrum 32 mass units less than those due to oligomers arising from intermolecular condensations only. Core-terminated species were recognized by the addition of the extra mass corresponding to the core moiety; however, it should be noted that this technique cannot distinguish between core-terminated species in which different numbers of core functionalities have reacted. The addition of an extra monomer unit to a core-terminated species results in a change of mass corresponding to the addition of a monomer residue minus the mass of a methanol unit, and the consequence for m/z is the same irrespective of whether the reaction is at the core or elsewhere in the oligomer. The MALDI spectra of the core-terminated polyesters showed peaks attributable to cyclic and core-terminated oligomers only. A comparison of the peak areas in the MALDI-TOF spectrum gave the relative amounts of each type of species, for a given degree of polymerization, which were then averaged for DP 4−8. The percentage of cyclic oligomers in a particular polymer was influenced by the relative amounts of core molecule used in the polymerization (Figure 7). Using 1 mol % of a B_3 core resulted in 78% cyclized polymer, but the fraction of cyclic polymer decreased when the core-to-monomer ratio was increased and above 10 mol % core incorporation there was virtually no cyclization. The B_3 core had a greater effect than the B_2 core, which is clearly attributable to the greater number of core B groups present, as shown in Figure 8. The core-terminated polymers effectively have no unreacted A groups as the focal groups have reacted either intramolecularly to form cycles or intermolecularly with other oligomers or core molecules. Thus, there should be no further opportunity for growth via polycondensation reactions. Hence, it is important to establish at what point in the reaction the complete consumption of A groups occurs. This was investigated by examining the MALDI spectra of core-terminated polyesters, produced using a fixed monomer: core ratio (0.0844), at different reaction times. After 5 h polymerization the product consisted of a mixture of uncyclized, cyclized, and core-terminated species in approximately equimolar amounts (Figure 9). The A groups were effectively consumed between 5 and 10 h polymerization, and after this point the proportions of cyclic and core-terminated polymer remained constant at around 50%. A comparison with the SEC data for the same system (Figure 10) shows that the number-average molecular weight remains fairly constant, but the weight-average molecular weight continues to increase after the point at which the A groups are fully consumed. This is consistent with the results obtained for the analogous AB_2 hyperbranched polyesters, reported previously, where the continual change in M_w was ascribed to the effect of ester interchange reactions.[14e]

Dilute Solution Viscometry. Viscosity measurements were made on solutions of the core-terminated hyperbranched polyesters in chloroform, at 25 °C, using an Ubbelhode viscometer. Experimentally, intrinsic viscosity, $[\eta]$, is often related to molecular weight by the empirical relationship most commonly known as the Mark−Houwink equation $[\eta] = KM^a$.[16] For many polymer systems there is a linear relationship between log-$[\eta]$ and log M_w, but for some dendritic macromolecules the Mark−Houwink plots exhibit maxima.[17] Mark−Houwink plots for the core-terminated polyesters gave good linear least-squares fits (correlation coefficients r^2 = 0.98−0.99) and are shown in Figure 11. The Mark−Houwink parameters are shown in Table 1 and are consistent with a branched polymer. The Mark−Houwink parameters are very similar irrespective of the core functionality and are in good agreement with those obtained for the analogous AB_2 polyester without a core.[14e] Linear Mark−Houwink plots have also been reported for other hyperbranched polyesters.[18]

Thermal Properties. The core-terminated hyperbranched polyesters were analyzed by differential scanning calorimetry (DSC). All samples showed a single

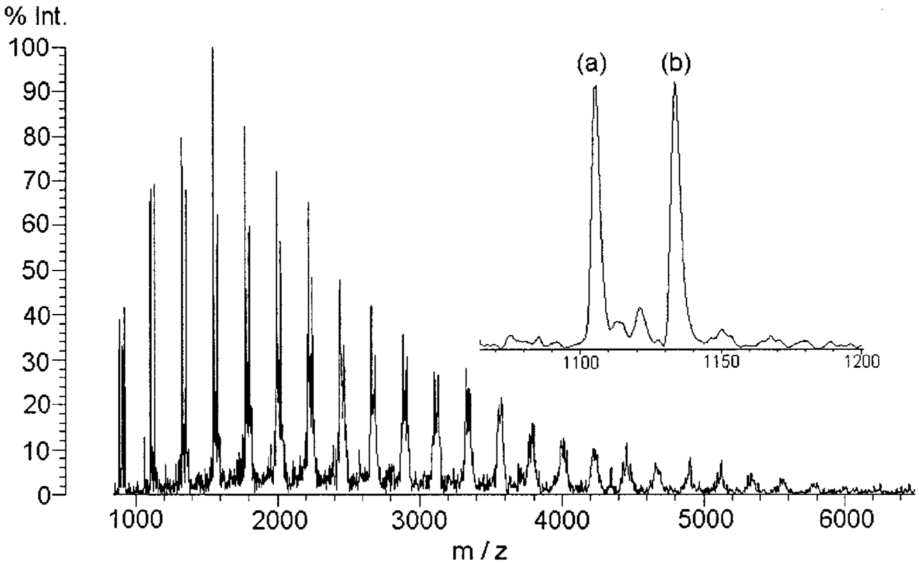

Figure 6. Typical MALDI spectrum for a B_2 core-terminated hyperbranched polyester. The inset shows the region corresponding to a degree of polymerization of 5: (a) oligomer containing four monomer residues plus a B_2 core molecule; (b) cyclic species containing five monomer residues.

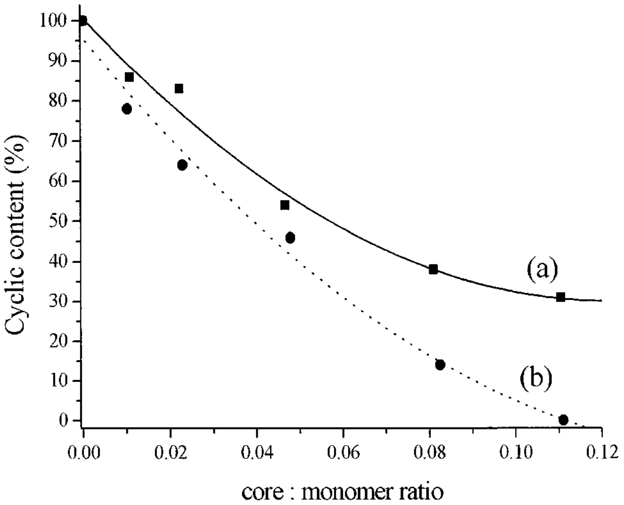

Figure 7. Variation of the cyclic content of core-terminated hyperbranched polyesters vs the core:monomer ratio: (a) B_2 core; (b) B_3 core.

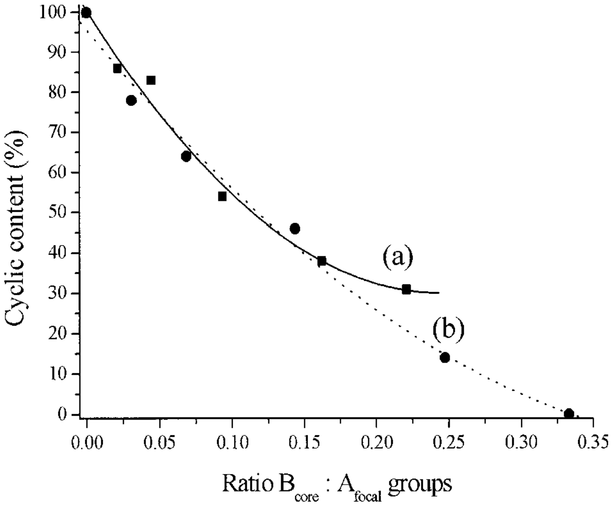

Figure 8. Effect upon the cyclic content of core-terminated hyperbranched polyesters of varying B_{core} group concentration: (a) B_2 core; (b) B_3 core.

glass transition with no evidence of melting or crystallization peaks. The glass temperature (T_g) tends toward a limiting value of 86 °C as the molecular weight is increased, as was observed for the analogous AB_2 polyesters.[14e] The dependency of the glass transition temperature of a linear polymer upon molecular weight can be described by chain end free volume theory using eq 1, where θ is the free volume of a single chain end, the number of chain ends per polymer molecule is 2, ρ is density, N_A is Avogadro's number, and α_f is the free volume expansion coefficient.[19]

$$T_g = T_g^{\infty} - \left(\frac{2\theta\rho N_A}{\alpha_f}\right)\left(\frac{1}{M_n}\right) \tag{1}$$

As $(2\theta\rho N_A/\alpha_f)$ is a constant, the glass transition temperature is proportional to $1/M_n$. It has been argued that such plots have little meaning for dendritic systems as the number of chain ends increases with molecular weight, and a modified free volume expression, such as eq 2, where η_e is the number of end groups, is more appropriate.[20]

$$T_g = T_g^{\infty} - \left(\frac{\theta\rho N_A}{\alpha_f}\right)\left(\frac{\eta_e}{M}\right) \tag{2}$$

However, this does not take into account the fact that the number of end groups in a hyperbranched or dendritic polymer is related to the degree of polymerization, and it has been shown that η_e/M is simply proportional to $1/M$.[14e] The glass transition temperature of the AB_2 hyperbranched polymer based upon dimethyl 5-(2-hydroxyethoxy)isophthalate, without a core, has been shown to be proportional to $1/M_w$. Plots of T_g against $1/M_w$ for the B_2 core-terminated and B_3 core-terminated hyperbranched polyesters also gave good linear least-squares fits (correlation coefficients $r^2 = 0.95$ and 0.98, respectively), shown in Figure 12. The core-terminated polymers have a limiting glass temperature of 86 °C, irrespective of core functionality. This is the same as the AB_2 hyperbranched polymer without a core, which is expected as the polymers all have the

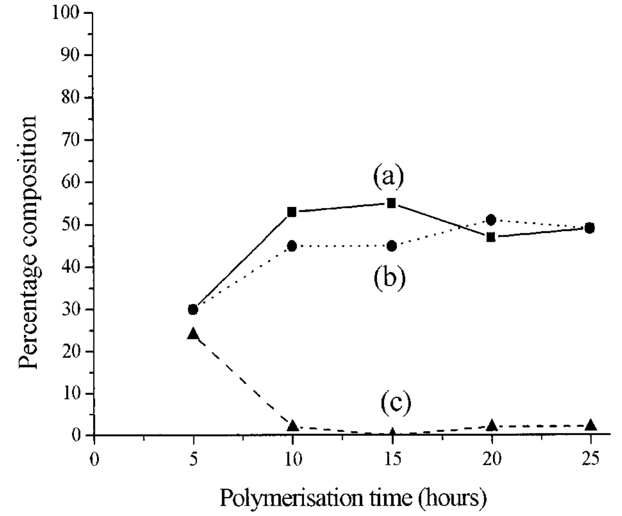

Figure 9. Variation of polymer composition with polymerization time for a core-terminated hyperbranched polyester. (a) core terminated, (b) cyclic, and (c) acyclic.

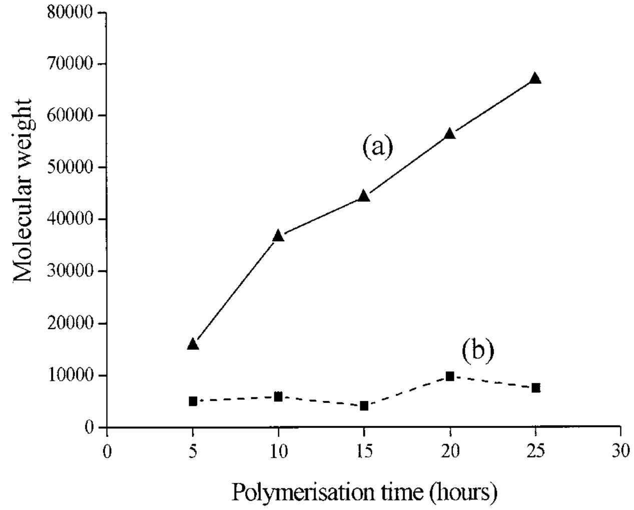

Figure 10. Variation of the molecular weight of a B_2 core-terminated hyperbranched polyester with reaction time (molecular weights from SEC in $CHCl_3$ with light scattering detector): (a) weight-average; (b) number-average.

same building blocks. The values for the glass temperature of the B_2 core-terminated polymers are lower than expected at high molecular weight. The slope of the line is related to the chain end free volume per unit volume of polymer. The hyperbranched polymers differ only in the type of focal group present, which may result in differences in the chain end free volume between the hyperbranched and core-terminated polymers. However, this seems an unlikely explanation for the differences in the slope as the B_3 core-terminated and the AB_2 system gave similar results, and the B_2 core only differs by a single methyl ester group. Currently we have no explanation for this experimentally reproducible anomaly.

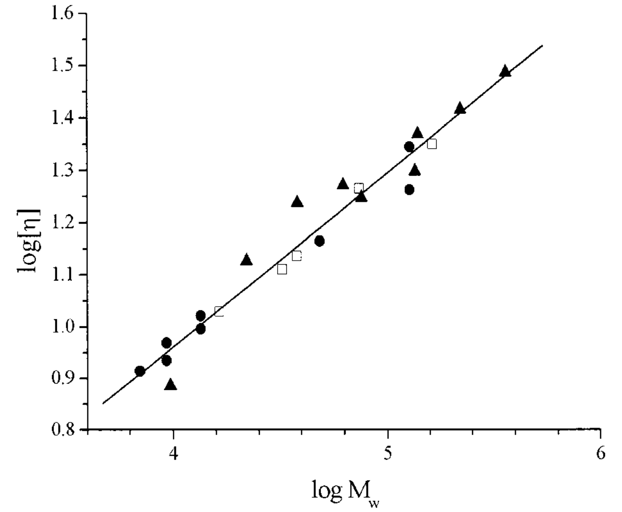

Figure 11. Mark–Houwink plots for core-terminated and hyperbranched polyesters (squares denote a B_2 core, circles a B_3 core and triangles no core).

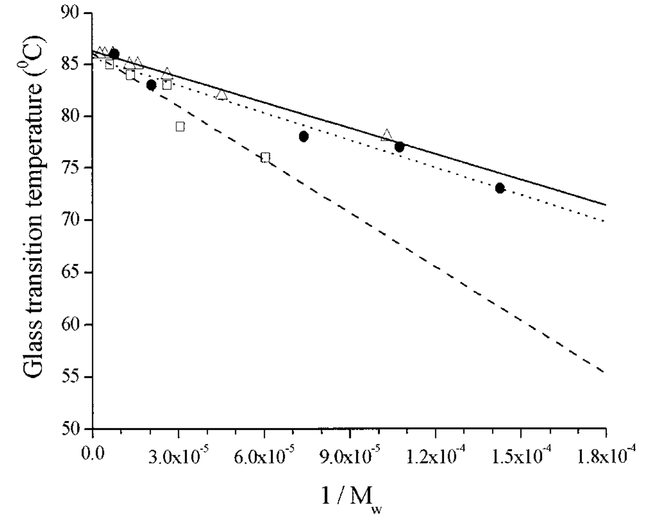

Figure 12. Variation of T_g with the reciprocal molecular weight for hyperbranched polyesters (squares denote a B_2 core, circles a B_3 core and triangles no core).

Table 1. Mark–Houwink Parameters for Core-Terminated and Hyperbranched Polyesters

polymer	a	K, cm^3 g^{-1}	r^2
AB_2 hyperbranched	0.3	0.6	0.98
B_2/AB_2 core-terminated	0.3	0.4	0.99
B_3/AB_2 core-terminated	0.3	0.6	0.98

Summary and Conclusions

Hyperbranched polyesters were prepared by condensation polymerization of the AB_2 monomer dimethyl 5-(2-hydroxyethoxy) isophthalate in the presence of either a B_3 core (trimethyl 1,3,5-benzenetricarboxylate) or a B_2 core (dimethyl isophthalate). These amorphous materials were highly soluble, relative to their linear analogues, in common organic solvents such as chloroform, yielding solutions with characteristically low intrinsic viscosities. A limited amount of control over the polymer molecular weight was achieved by varying the core:monomer ratio used in the polymerization. There would appear to be no significant difference between the core molecules studied here other than that the higher functionality B_3 core provides a greater number of B groups and hence potential core-terminating reactions. A groups are consumed in the polymerization by polycondensation, cyclization, or core termination, the latter two processes effectively preventing further growth by a polycondensation mechanism. The polyester's weight-average molecular weight continues to increase even after complete consumption of A groups, which is presumably a result of ester exchange processes. Hence, there is no control over the polydispersity, at protracted reaction times, by the introduction of a core in this system.

References and Notes

(1) Sunder, A.; Heinemann, J.; Frey, H. *Chem. Eur. J.* **2000**, *6*, 2499.

(2) (a) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953. (b) Burchard, W. *Adv. Polym. Sci.* **1999**, *143*, 113.

(3) Flory, P. J. *J. Am. Chem. Soc.* **1952**, *74*, 2718.

(4) Müller, A. H. E.; Yan, D.; Wulkow, M. *Macromolecules* **1997**, *30*, 7015.

(5) Feast, W. J.; Stainton, N. M. *J. Mater Chem*. **1995**, *5*, 405.

(6) Lach, C.; Müller, P.; Frey, H.; Mülhaupt, R. *Macromol. Rapid Commun*. **1997**, *18*, 253.

(7) Hobson, L. J.; Feast, W. J.*Polymer* **1999**, *40*, 1279.

(8) Malmström, E.; Johansson, M.; Hult, A. *Macromolecules* **1995**, *28*, 1698.

(9) (a) Yan, D.; Zhou, Z. *Macromolecules* **1999**, *32*, 819. (b). Zhou, Z.; Yan, D. *Polymer* **2000**, *41*, 4549.

(10) (a) Holter, D.; Frey, H. *Acta Polym*. **1997**, *48*, 298. (b) Hanselmann, R.; Hölter, D.; Frey, H. *Macromolecules* **1998**, *31*, 3790. (c) Radke, W.; Litvinenko, G.; Müller, A. H. E. *Macromolecules* **1998**, *31*, 239. (d) Widmann, A. H.; Davies, G. R. *Comput. Theor. Polym. Sci.* **1998**, *8*, 191.

(11) Sunder, A.; Hanselmann, R.; Frey, H.; Mülhaupt, R. *Macromolecules* **1999**, *32*, 4240.

(12) Barathi, P.; Moore, J. S. *Macromolecules* **2000**, *33*, 3212.

(13) Gong, C.; Miravet, J.; Fréchet, J. M. J. *J. Polym. Sci., Part A: Polym. Chem*. **1999**, *37*, 3193.

(14) (a) Percec, V.; Chu, P.; Kawasumi, M. *Macromolecules* **1994**, *27*, 4441. (b) Feast, W. J.; Keeney, A. J.; Kenwright, A. M.; Parker, D. *J. Chem. Soc., Chem. Commun*. **1997**, 1749. (c) Gooden, J. K.; Gross, M. L.; Mueller, A.; Stefanescu, A. D.; Wooley, K. L. *J. Am. Chem. Soc.* **1998**, *120*, 10180. (d) Dušek, K.; Šomvársky, J.; Smrčková, M.; Simonsick, W. J.; Wilczeck, L. *Polym. Bull.* **1999**, *42*, 489. (e) Parker, D.; Feast, W. J. *Macromolecules* **2001**, *34*, 2048.

(15) Burgath, A.; Sunder, A.; Frey, H. *Macromol. Chem. Phys.* **2000**, *201*, 782.

(16) Mays, J. W.; Hadjichristidis, N. In *Modern Methods of Polymer Characterisation*; Barth, H. G., Mays, J. W., Eds.; Wiley-Interscience: New York, 1991; p 233.

(17) (a) Tomalia, D. A.; Hedstrand, D. M.; Wilson, L. R. In *Encyclopaedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley-Interscience: NewYork, 1990; Index Volume. (b) Mourey, T. H.; Turner, S. R.; Rubinstein, M.; Fréchet, J. M. J.; Hawker, C. J.; Wooley, K. L. *Macromolecules* **1992**, *25*, 2401. (c) de Brabander-van den Berg, E. M. M.; Nijenhuis, A.; Mure, M.; Keulen, J.; Reintjens, R.; Vandenbooren, F.; Bosman, B.; de Raat, R.; Frijns, T.; van den Wal, S.; Castelijns, M.; Put, J.; Meijer, E. W. *Macromol. Symp*. **1994**, *77*, 51.

(18) (a) Turner, S. R.; Voit, B. I.; Mourey, T. H. *Macromolecules* **1993**, *26*, 4617. (b) Turner, S. R.; Walter, F.; Voit, B. I.; Mourey, T. H. *Macromolecules* **1994**, *27*, 1611.

(19) Bueche, F. *Physical Properties of Polymers*; Interscience: New York, 1962.

(20) Wooley, K. L.; Hawker, C. J.; Pochan, J. M.; Fréchet, J. M. J. *Macromolecules* **1993**, *26*, 1514.

MA010502C