Macromolecules **2001,** *34,* 2048−2059

Synthesis, Structure, and Properties of 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 October 31, 2000

ABSTRACT: The melt condensation polymerization of the AB_2 monomer dimethyl 5-(2-hydroxyethoxy)-isophthalate exhibits unusual molecular weight growth characteristics. The number-average molecular weight (M_n) reaches a plateau value after a relatively short polymerization time, whereas the weight-average molecular weight (M_w) continues to increase. The maximum in M_n is thought to be a consequence of intramolecular cyclization reactions, evidence of which is provided by MALDI-TOF MS. It is postulated that the continual increase in weight-average molecular weight, even after complete cyclization, is due to a redistribution of polymer chains by ester interchange reactions. The polymers are soluble in common organic solvents, and solutions have characteristically low intrinsic viscosities. The degree of branching, as determined by quantitative ^{13}C NMR spectroscopy, is consistent with the theoretical value for a statistical distribution at high conversion. The physical characterization of these polymers is reported.

Introduction

Dendritic macromolecules can be divided into two types: dendrimers and hyperbranched polymers.[1] Dendrimers, which are well-defined monodisperse regular structures in which all branch points are utilized, often exhibit unusual and attractive properties but are made using laborious iterative syntheses. In contrast, hyperbranched polymers are usually made in one-pot reactions. They may be considered as irregular analogues of dendrimers and are consequently less well-defined polydisperse systems with varying degrees of branching. To date, the majority of hyperbranched polymers have been made using step growth polycondensation reactions employing monomers of AB_x type, where A and B represent two different functional groups and x is the number of B groups in the monomer. Polymerization proceeds by the reaction of A groups with B groups and leads to structures such as that shown in Figure 1.

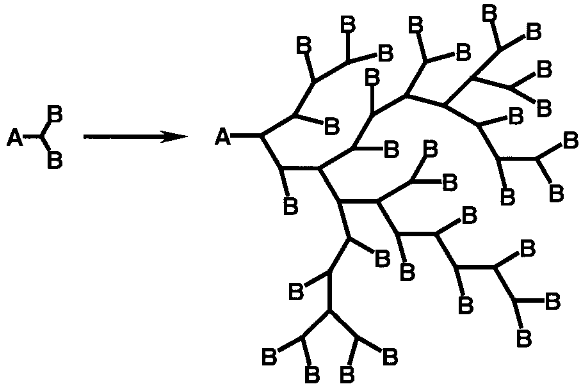

Figure 1. Schematic representation of an AB_2 type polymerization.

Molecular weight distributions in polyfunctional condensations were first studied by Flory in the 1950s using a statistical approach that assumes that all B groups are of equal reactivity.[2] A further assumption is that intramolecular condensation reactions do not occur, and hence each oligomer contains a single A group and many B groups. The number of B groups in a given oligomer is dependent upon the degree of polymerization (DP), and for an AB_2 system the number of B groups is given by DP + 1. This favors growth of the larger oligomers, and according to this model, as the reaction proceeds, the weight-average degree of polymerization, x_w, increases much faster than the number-average, x_n. As the extent of reaction approaches unity, the polydipersity index (x_w/x_n) is predicted to approach infinity; hence, AB_x type polymers are expected to have very broad molecular weight distributions at high conversion. Although theoretical treatments and kinetic analyses are often simplified by neglecting intramolecular cyclization reactions,[2,3] there is an increasing body of evidence demonstrating that this is not always a realistic assumption. Percec and co-workers reported the first example of cyclization in hyperbranched polymers.[4] Subsequently, an increasing number of hyperbranched systems have been examined for the presence of cyclic species.[5] These systems vary considerably in cyclic content, and it is apparent that the outcome of AB_x step growth polymerizations is a sensitive function of monomer structure and reaction conditions. The complete consumption of A groups by the competitive processes of polymerization and cyclization has been reported to be responsible for the observed maximum attainable molecular weight in some hyperbranched polymerizations.[5a,f] This is a marked deviation from the growth behavior predicted by Flory (see Figure 2). We report here the occurrence of cyclization leading to unusual molecular growth behavior of polymers derived from the AB_2 monomer dimethyl 5-(2-hydroxyethoxy)isophthalate (Figure 3).

In an idealized AB_2 type polymer linear (L), dendritic (D), and terminal (T) structural units may be identified. Terminal units are those that retain both B groups and linear units contain a single unreacted B group whereas dendritic units have no unreacted B functionalities. As the incorporation of a dendritic unit adds a new growth direction, ultimately ending in a terminal group, each polymer molecule should contain one more terminal unit than the number of dendritic units. The relative proportions of these structural units have been used as a

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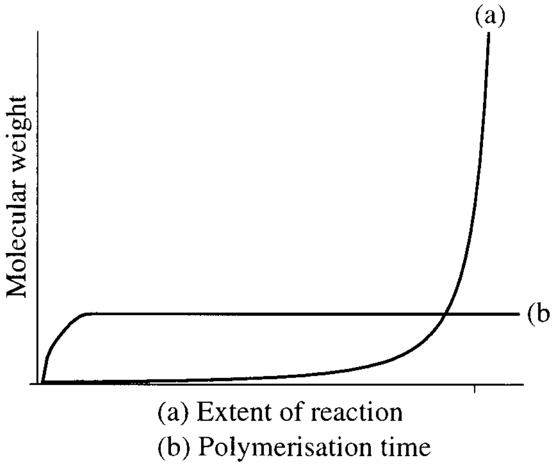


Figure 2. Schematic representation of molecular weight growth for AB_x type polymerizations: (a) theoretical statistical growth;[2] (b) observed behavior of some cyclized systems.[5a,f]

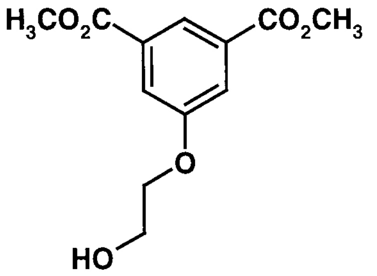


Figure 3. AB_2 monomer dimethyl 5-(2-hydroxyethoxy)isophthalate.

means of evaluating the branching content of hyperbranched polymers, and the degree of branching has been defined as the ratio of actual growth directions to the maximum possible number of growth directions, as shown in eq 1, where L and D are the sums of the linear and dendritic units, respectively.[3b]

$$\mathrm{DB} = \frac{D}{D_{\max}} = \frac{2D}{2D + L} \qquad (1)$$

The degree of branching is proportional to the extent of reaction (p_A) and for an AB_2 system DB = $0.5p_A$; consequently, the theoretical maximum DB for a statistical growth of an AB_2 polymer is 0.5.[6]

While the evaluation of branching within hyperbranched polymers is clearly desirable, it does not necessarily provide useful information about their overall topology. For example, a degree of branching of one does not imply regular polymer growth but merely the absence of linear sections within the structure. Hence, a dendrimer by definition has a DB of one but the converse is not true, and nondendritic structures, including essentially linear molecules, may also have degrees of branching equal to one. Furthermore, many isomeric structures are possible for a polymer molecule with a given degree of branching.[7]

Experimental Section

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

Instrumentation. Melting points were obtained using an Electrothermal IA9200 series digital melting point apparatus. Elemental analyses were obtained using an Exeter analytical elemental analyzer CE-440. Infrared spectra were obtained on a Perkin-Elmer 1720X FTIR spectrometer. ^1H and ^{13}C NMR spectra were acquired on either a Varian Unity 300 spectrometer at 299.91 MHz (^1H) and 75.41 MHz (^{13}C) or a Varian Inova 500 at 500.14 MHz (^1H) and 125.77 MHz (^{13}C). ^{13}C NMR spectra at 100 °C in tetrachloroethane-d_2 were acquired on a Varian Inova 500, using relaxation delays of 2 and 4 s (spectra were identical, as required for quantitative integration). Mass spectra of the monomer and its precursor were recorded on a Micromass AutoSpec instrument. Mass spectra of the polymers 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 PL gel 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. The refractive index increment was determined in both chloroform and THF using a Brice-Phoenix differential refractometer. 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.

Synthesis of Dimethyl 5-Hydroxyisophthalate. Anhydrous hydrogen chloride (38.5 g, 1.04 mol) was bubbled through a stirred mixture of 5-hydroxyisophthalic acid (275.0 g, 1.51 mol) and methanol (1300 cm^3) to form a clear solution. The solution was heated under reflux for 4 h, and on cooling to room temperature the crude product crystallized from the methanol solution as a white solid. The solid was recovered by filtration, washed with cold water, and recrystallized from methanol to yield dimethyl 5-hydroxyisophthalate (258.0 g, 1.23 mol, 81%) as fine colorless needles (mp 158 °C, lit.[8] 158–159 °C). Analysis by thin-layer chromatography (silica gel/ethyl acetate) showed a pure compound (single spot, R_f = 0.73). Elemental analysis calculated for $C_{10}H_{10}O_5$: C, 57.14%; H, 4.80%. Found: C, 56.84%; H, 4.78%. FTIR (KBr disk): λ_{max}: 3363, 3011, 2961, 1703, 1599, 756 cm^{-1}. ^1H NMR (acetone-d_6, 300 MHz): δ 3.91 (s, 6H, OCH_3), δ 7.67 (d, 2H, ArH). δ 8.08 (t, 1H, ArH). ^{13}C NMR (acetone-d_6, 75 MHz): δ 52.01 ($C$$H_3$), δ 120.42, 121.33 (aromatic C–H), δ 132.18 (aromatic C–R), δ 158.02 (aromatic C–O), δ 165.80 (C=O). MS (EI+): 210 (M), 179 (M–OCH_3), 151 (–CO_2CH_3), 136 (M–CH_3, –CO_2CH_3). These spectral data were consistent with those reported.[8]

Synthesis of Dimethyl 5-(2-Hydroxyethoxy)isophthalate. A 2 L pressure reactor was charged with dimethyl 5-hydroxyisophthalate (100.0 g, 0.48 mol), sodium methoxide (6.0 g, 0.17 mol), ethylene oxide (44.0 g, 1.00 mol), and methanol (600 cm^3). The vessel was pressurized with 100 psi of nitrogen and the solution stirred at 95 °C for 6 h. The product, obtained as a white solid, was recovered by filtration, washed with water, recrystallized from a mixture of methanol and water (50% v/v), and dried in a vacuum oven (yield 95.2 g, 0.37 mol, 78%; mp 109.8–110.2 °C, lit.[8] 112.0–112.5 °C). Single spot in TLC analysis (silica gel 60, ethyl acetate R_f = 0.55). Calculated for $C_{12}H_{14}O_6$: C, 56.69%; H, 5.55%. Found: C, 56.62%; H, 5.56%. FTIR (KBr disk) λ_{max}: 3312, 3010, 2951, 1727, 1596, 754 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.38 (s, 1H, OH), δ 3.94 (s, 6H, OCH_3), δ 4.01 (t, 2H, CH_2), δ 4.18 (t, 2H, CH_2), δ 7.76 (d, 2H, ArH), δ 8.28 (t, 1H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 52.70 ($C$$H_3$), δ 61.42, δ 70.04 (aliphatic

*C*H$_2$), δ 120.05, δ 123.51 (aromatic *C*−H), δ 132.00 (aromatic *C*−R), δ 158.93 (aromatic *C*−O), δ 166.26 (*C*=O). MS (EI+): 254 (M), 223 (M−OCH$_3$), 211 (M−CH$_2$CH$_2$OH), 210 (M−CH$_2$=CHOH), 179 (M−CH$_2$=CHOH, −OCH$_3$), 151 (−CO$_2$CH$_3$), 136 (M−CH$_3$, −CO$_2$CH$_3$).

Representative Polymerization Procedure. Dimethyl 5-(2-hydroxyethoxy)isophthalate (5.0 g, 19.69 mmol), Mn(OAc)$_2$ (3.2 mg, 0.018 mmol), Sb$_2$O$_3$ (2.1 mg, 0.007 mmol), and (PhO)$_3$PO (2.7 mg, 0.008 mmol) were heated at a rate of 10 °C/min to 240 °C and held at that temperature for a period of 4 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 clear brown brittle glass (3.5 g). No purification of the polymer was carried out at this stage. SEC (CHCl$_3$, polystyrene equivalents): M_w 37 900, M_w/M_n 5.3. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 3.89 (br s, OC*H*$_3$), δ 4.39, δ4.70 (br s, C*H*$_2$), δ 7.75 (br s, Ar*H*), δ 8.24 (br s, Ar*H*). ^{13}C NMR (tetrachloroethane-*d*$_2$, 125 MHz): δ 52.21 (s, *C*H$_3$), δ 63.55, δ 67.06 (s, aliphatic *C*H$_2$), δ 120.44, δ 123.77 (m, aromatic *C*−H), δ 132.24 (m, aromatic *C*−R), δ 158.90 (s, aromatic *C*−O), δ 165.48 (m, *C*=O).

Results and Discussion

A series of hyperbranched polyesters have been prepared by melt condensation polymerization of the AB$_2$ monomer dimethyl 5-(2-hydroxyethoxy)isophthalate. The synthesis of the monomer from 5-hydroxyisophthalic acid was accomplished using a modified version of the route reported by Turner and co-workers.[9] Esterification of 5-hydroxyisophthalic acid was followed by addition of the resulting dimethyl 5-hydroxyisophthalate to ethylene oxide. We were unable to repeat this reaction using the conditions previously reported,[9] but the addition of a small amount of sodium methoxide and the use of methanol as solvent gave high yields of the required AB$_2$ monomer. Polymerization of the AB$_2$ monomer 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 time in the melt. The resulting polymers were obtained as brittle brown glasses that were readily soluble in chloroform.

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). Other research groups have reported the characterization of hyperbranched polymers using multidetector systems incorporating low-angle light scattering.[10] The use of a light scattering detector required the determination of the specific refractive index increment, d*n*/d*c*, which was measured using a differential refractometer. The polymers were analyzed as solutions in both chloroform (d*n*/d*c* 0.123 cm^3 g^{-1}) and tetrahydrofuran (d*n*/d*c* 0.141 cm^3 g^{-1}). The SEC chromatograms revealed broad molecular weight distributions, becoming both broader and polymodal in character with increasing polymerization time (Figure 4). The polymodal character of the chromatograms was unanticipated but in agreement with similar work reported by Turner et al.[9,10] The presence of additional peaks due to very high mass species was revealed by the light scattering detector; however, this type of detector emphasizes higher molecular weight species, and the extra peaks only represent a very small amount of material, as shown by the RI detector response in Figure 5. These extra peaks, which are possibly due to aggregation, were deemed to represent only a very minor component and have been omitted from the calculation of average molecular weights. No extra peaks were observed using SEC in chloroform, which is a better solvent for these polymers, and the results from the light scattering detector are in reasonable agreement using both solvent systems. A comparison of the results using the various detector systems is shown in Figure 6. Molecular weights obtained using conventional polystyrene calibration are generally higher for polymer solutions in chloroform than in THF, consistent with chloroform being the better solvent. The molecular weights obtained by conventional polystyrene calibration, in either solvent, are appreciably lower than those obtained by either universal calibration or light scattering. The results obtained by universal calibration are in reasonable agreement with those from the light scattering detector although any differences are greatest for the higher molecular weight samples. A good agreement between molecular weights obtained by light scattering and universal calibration has been observed in other hyperbranched polyesters.[9]

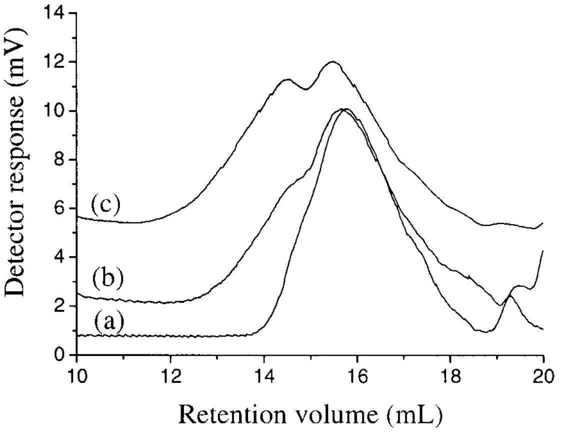


Figure 4. SEC chromatograms (CHCl$_3$ eluent, RI detector, column sets as detailed in the Experimental Section) for the hyperbranched polyesters after (a) 2 h, (b) 8 h, and (c) 24 h polymerization.

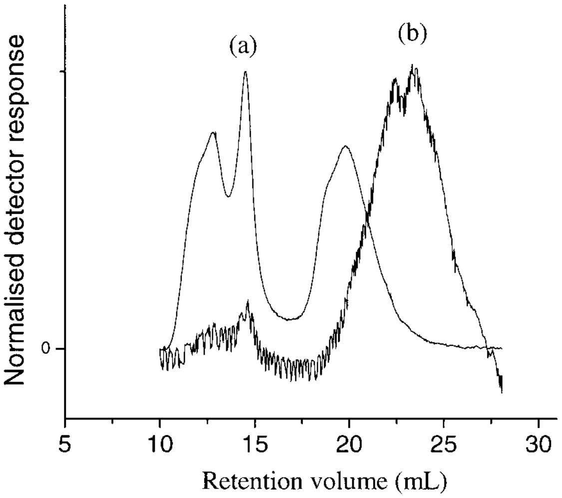


Figure 5. Comparison of RI and RALLS detector response (THF eluent, column sets as detailed in the Experimental Section) for a hyperbranched polyester after 24 h polymerization: (a) RALLS detector; (b) RI detector.

As expected, there is a trend of increasing M_w with increasing reaction time leading to very large values of polydispersity (M_w/M_n). However, the number-average

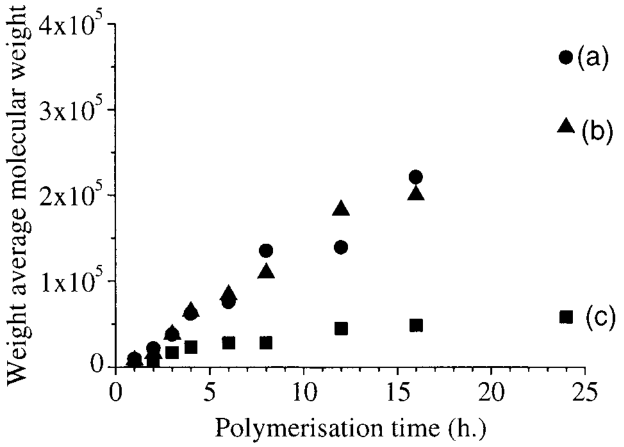


Figure 6. Comparison of SEC results for the hyperbranched polyesters using different SEC detectors: (a) DV (universal calibration); (b) RALLS-DV-RI; (c) RI (conventional polystyrene calibration).

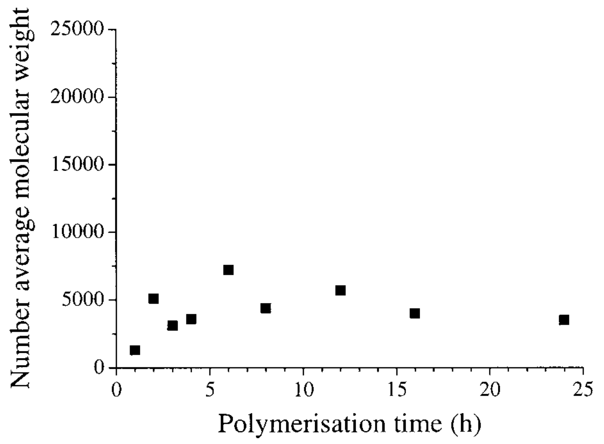


Figure 7. Variation of number-average molecular weight with polymerization time.

molecular weight does not continue to rise but reaches a maximum value after relatively short reaction times (Figure 7). This limit to M_n has been observed in other hyperbranched systems and has been ascribed to intramolecular cyclization; an associated maximum in M_w is observed in these cases.[5a,f]

Dilute Solution Viscometry. Viscosity measurements were made using the SEC differential viscometer and by conventional capillary viscometry using an Ubbelhode viscometer. The intrinsic viscosity data for hyperbranched polymers in chloroform obtained from SEC are slightly lower than those obtained for the same samples by capillary viscometry, which is probably due to the higher temperature used in SEC. Experimentally, intrinsic viscosity, $[\eta]$, is often related to molecular weight by the empirical relationship most commonly known as the Mark–Houwink equation $[\eta] = KM^a$.[11] Mark–Houwink plots ($\log[\eta]$ vs $\log M_w$) gave good linear least-squares fits (correlation coefficients $r^2 = 0.92$–0.99) and are shown in Figure 8. The Mark–Houwink parameters are shown in Table 1 and are consistent with a branched polymer. The Mark–Houwink plot across the whole molecular weight distribution was obtained directly from the SEC viscometer and was also linear as shown in Figure 9. The linear Mark–Houwink plots obtained for the hyperbranched polyesters are consistent with the reported behavior of other hyperbranched polyesters, such as those derived from (dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s,[12] 5-acetoxyisophthalic acid, or 1,3-diacetoxybenzoic acid,[9,10] but unlike those for dendrimers[13] and one hyperbranched polyamidoamine[7a] which exhibit maxima.

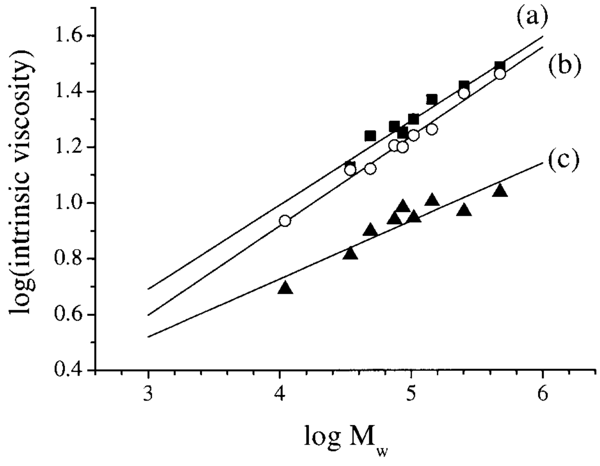


Figure 8. Mark–Houwink plots for hyperbranched polyesters: (a) Ubbelhode viscometer, $CHCl_3$; (b) SEC viscometer, $CHCl_3$; (c) SEC viscometer, THF.

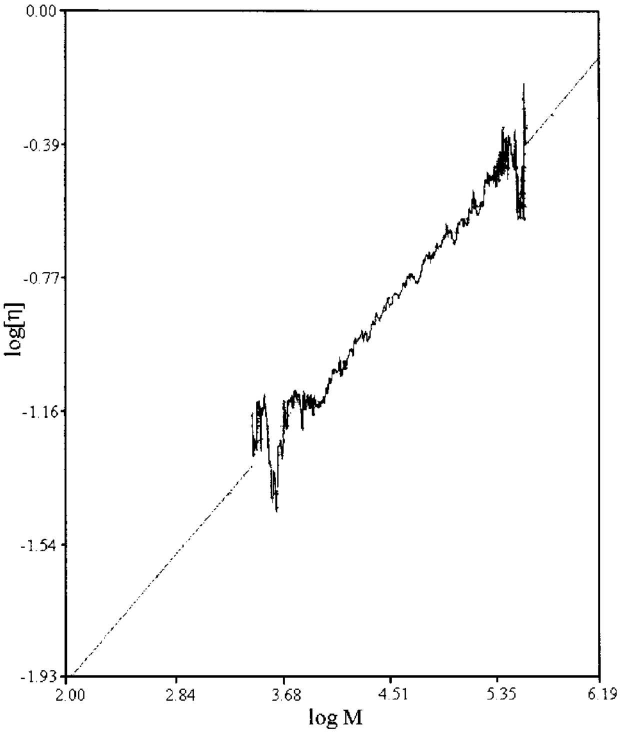


Figure 9. Representative Mark–Houwink plot for a hyperbranched polyester (M_w 49 000, $CHCl_3$ at 30 °C) from SEC.

Table 1. Mark–Houwink Parameters for Hyperbranched Polyesters

viscometer	solvent	temp (°C)	a	K (cm^3 g^{-1})	r^2
Ubbelhode	$CHCl_3$	25	0.3	0.6	0.98
SEC	$CHCl_3$	30	0.3	0.4	0.99
SEC	THF	30	0.2	0.8	0.92

Cyclization. To investigate further the molecular weight growth of the hyperbranched polyesters, dimethyl 5-(2-hydroxyethoxy)isophthalate was polymerized for 65 h, without a catalyst, sampled every 5 h, and analyzed using MALDI-TOF mass spectroscopy. A MALDI-TOF MS spectrum representative of those obtained from the hyperbranched polyesters is shown

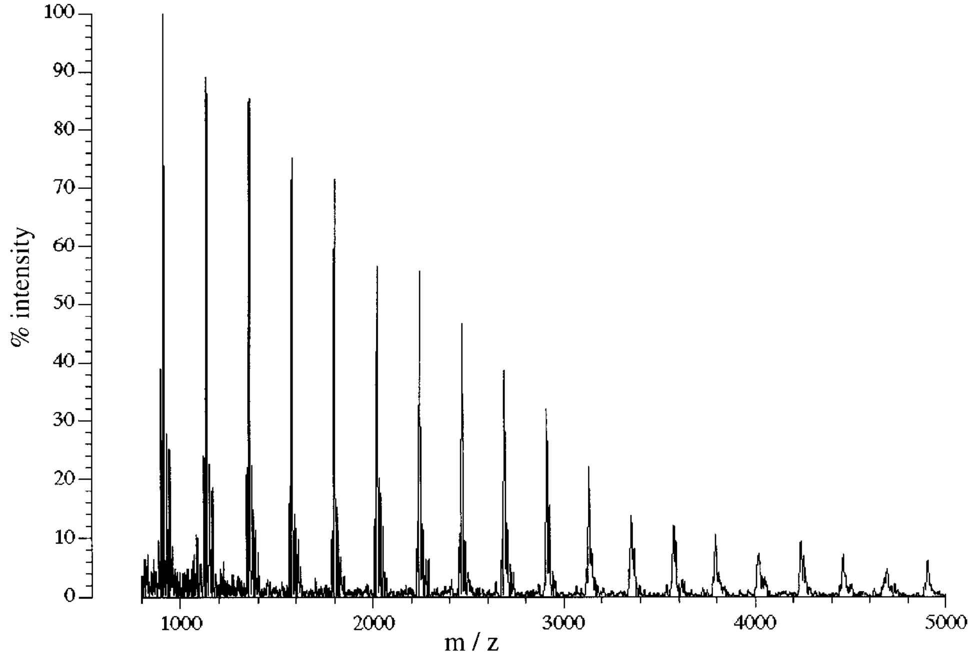


Figure 10. MALDI-TOF spectrum of a hyperbranched polyester after 10 h polymerization.

in Figure 10. The MALDI-TOF MS spectrum shows a series of peaks corresponding to a distribution of oligomers with increasing degrees of polymerization up to a DP of 22. It is apparent that the high molecular weight region of the spectrum is under represented, and molecular weight averages calculated from the MALDI-TOF spectra are much too low. For example, analysis of the MALDI-TOF spectrum of the hyperbranched polyester prepared in a 50 h polymerization gave a number-average molecular weight of 2300 and a polydispersity (M_w/M_n) of 1.2. The corresponding values from SEC were M_n 8000 (polystyrene equivalent molecular weight) and M_w/M_n 14.6. The failure of MALDI-TOF MS to give reliable molecular weight averages for polymers with broad molecular weight distributions has been widely reported.[14,15] It has been shown that in a polydisperse sample the optimum laser power required for the ionization/desorption process is greater for the high molecular weight species than the low molecular weight oligomers. The greater levels of laser power required for the analysis of high molecular weight species can lead to fragmentation of lower DP components. Although it was not possible to obtain reliable molecular weight averages for the hyperbranched polyesters by MALDI-TOF MS, it was possible to obtain the masses of individual oligomers in the low molecular weight region. The hyperbranched polyesters were examined with the addition of KCl to the matrix, and individual species in the MALDI-TOF spectrum were observed as the parent species plus an attached cation $[M + K]^+$. With this instrument and matrix the region below a DP of 4 is obscured by matrix and fragmentation peaks while peaks corresponding to a DP of greater than 11 are not fully resolved. Hence, the analysis of the MALDI-TOF spectra was restricted to the region associated with DP 4−11 (*m*/*z* 900−2600). The mass of a particular oligomer may be calculated by a consideration of the polymerization process. An oligomer of *n* repeat units is the result of $(n - 1)$ condensation steps. 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 main ion series observed for the hyperbranched polymers prepared with short polymerization times corresponded to oligomers formed by such successive condensation reactions. However, two further ion series were also present as shown in Figure 11. The first of these was observed 32 mass units behind the main series and can be attributed to the loss of a further single methanol moiety to form a cyclic polymer. An alternative interpretation of this series would be hydrolysis of a single methyl ester unit. If this is occurring, it seems reasonable to expect that more than one of the many methyl ester units in each molecule would undergo the reaction, but there is no evidence for the extra methanol losses required. The second extra ion series is observed 44 mass units behind the main series. This can be explained by cleavage of the alkyl chain of the focal group at the O−C bond β to the aromatic ring accompanied by a hydrogen migration. This is a common fragmentation of aromatic alkyl ethers in electron impact mass spectrometry.[16] The fragmentation of hyperbranched polymers leading to loss of a focal point group has been observed in the MALDI-TOF MS of hyperbranched poly(amidoamines).[7a] The proportion of oligomers due to cyclized polymer increased with longer reaction times. The disappearance of the series of ions due to hyperbranched polymer minus the focal group, in the spectra of the polymers after long reaction times, supports the notion that the fragmentation occurs in the spectrometer and not during the polymerization. If it occurred during the polymerization, such species would be expected to be present in all samples, whereas if the fragmentation occurs in the spectrometer, this can only occur in samples with significant amounts of uncyclized material present. Comparing the peak areas in the MALDI-TOF spectrum gave the relative amount of each type of species, for a given degree of polymerization. The percentage cyclic content of the oligomers, corresponding to DP 4−11, was constant across the region of the spectrum examined. The variation in average cyclic content with polymerization time is shown in Figure 12. The proportion of cyclic polymer increases with increasing polymerization time until all

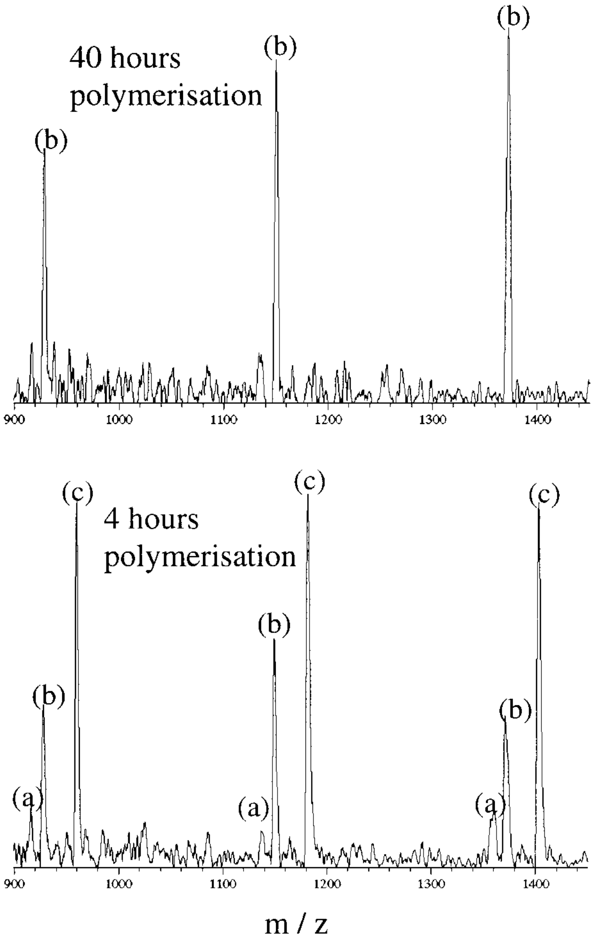


Figure 11. MALDI-TOF spectra of potassium-doped hyperbranched polyester after 4 and 40 h polymerization. Only the region corresponding to degree of polymerization 4–6 is shown. (a) Hyperbranched polymer minus focal group. (b) Hyperbranched polymer containing cycle. (c) Hyperbranched polymer.

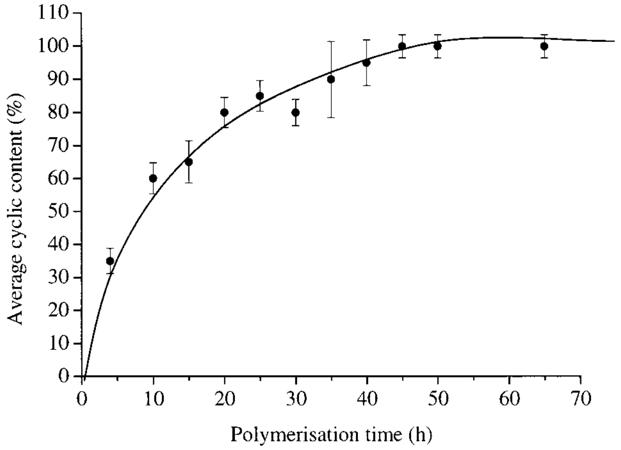


Figure 12. Variation of average cyclic content of hyperbranched polyesters, in the range DP 4–11, with polymerization time.

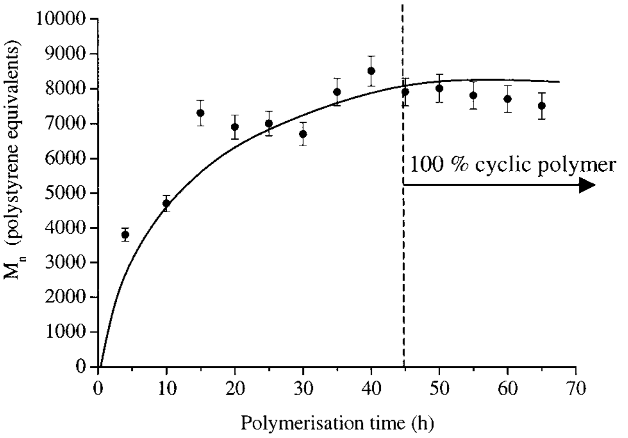


Figure 13. Effect of cyclization upon M_n for hyperbranched polyesters.

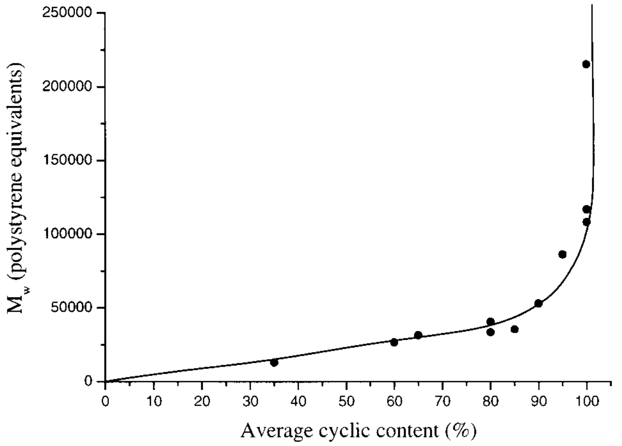


Figure 14. Variation of M_w with cyclic content for hyperbranched polyesters.

the oligomers, between DP 4 and 11, are fully cyclized after 45 h reaction. The number of monomer residues in the cyclic portion of a given oligomer cannot be determined by MALDI-TOF MS;[17] however, oligomers as low as DP 4 contain a cyclic part, and the ring size in these species must necessarily be small. Oligomers lower than DP 4 cannot be identified with any certainty in the MALDI-TOF spectrum, but cyclic oligomers as small as DP 2 are feasible. Similarly, it is unknown whether oligomers of DP $\gg$ 11 contain cycles, but the nature of step growth polymerization would suggest this is likely. Higher oligomers are created by oligomer/oligomer or oligomer/monomer condensation reactions. As many of the lower DP oligomers are cyclized, then it is probable that the higher molecular weight species are also cyclized. Dušek has reported a kinetic simulation of AB_2 polymerization, which suggests that if cyclization occurs, at high extents of reaction, the higher molecular weight oligomers are all cyclized.[5g] Other modeling studies suggest that statistically cyclization is the likely outcome of hyperbranched polymerizations.[18]

The point at which those oligomers measurable by MALDI-TOF MS are fully cyclized corresponds to the observed limit in the number-average molecular weight, as shown in Figure 13. A fully cyclized AB_2 polymer has no remaining A groups left to undergo condensation reactions, and hence further growth is not possible by this mechanism. Cyclization leading to growth termination has been observed in hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s[5a,12] and hyperbranched poly(siloxysilane)s.[5f] In both these cases the limit to the maximum attainable M_n was also accompanied by a maximum in the value of M_w. Surprisingly, this is not the case with the hyperbranched polyesters described here as the weight-average molecular weight, shown in Figure 14, continues to increase after complete cyclization. Clearly such continued growth must be via an alternative mechanism to simple condensation polymerization.

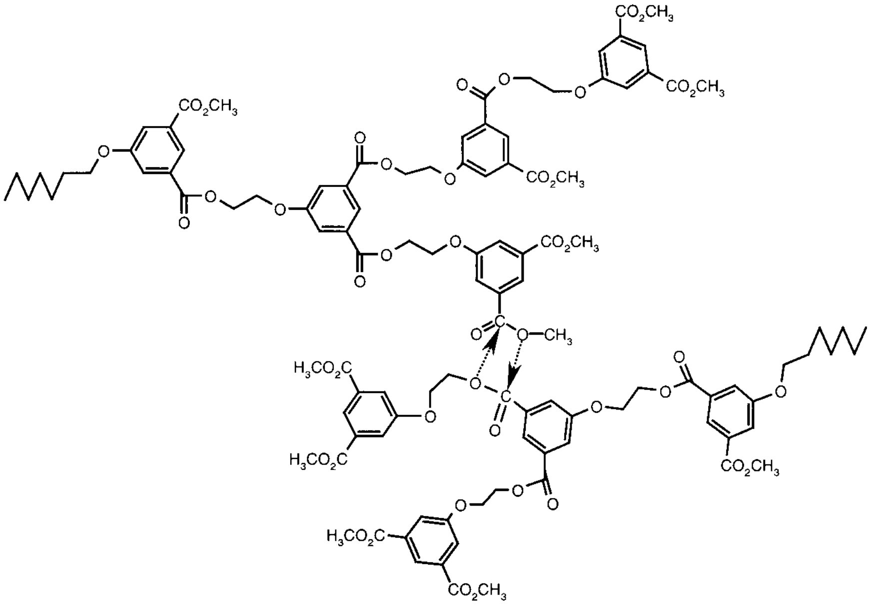


Figure 15. Ester interchange reaction between hyperbranched polyesters.

Transesterification. Molten polyesters readily undergo interchange reactions in which the polymer chains undergo the scission and recombination reactions collectively referred to as transesterification.[19] Three types of interchange reaction may be identified and are termed alcoholysis, acidolysis, and ester interchange,[20] although the relative contribution of these processes to transesterification is the subject of current debate. The contribution of alcoholysis, which is believed to be the faster process,[21] has been demonstrated in blends of poly(ethylene terephthalate) and poly(ethylene naphthalene-2,6-dicarboxylate).[19,22] There is less evidence for direct ester interchange, but it is believed to be the slower process[21] and has been demonstrated in blends of poly(butylene terephthalate) and bisphenol A polycarbonate.[23] In the case of the hyperbranched polyesters, the alcoholysis reaction is the reaction responsible for polycondensation and cannot take place after all the hydroxyl A groups are consumed by polycondensation and/or cyclization reactions. Within the limits of our analytical techniques, no acid groups are detectable in this system, and hence, it is likely that acidolysis can be disregarded as a potential interchange reaction. However, it is possible that the observed changes in the molecular weight distribution are the result of direct ester interchange reactions between hyperbranched polyesters molecules. An interchange reaction between two similar sized polymer molecules to produce one much larger and one correspondingly smaller molecule will contribute toward an increase in the weight-average molecular weight. Conversely, the reaction between one large and one small molecule to produce two intermediate size molecules will contribute to a decrease in the weight-average molecular weight. If the weight-average molecular weight of the bulk sample is to increase, then the contribution of reactions producing different size molecules must outweigh the contribution from reactions producing similar size molecules. This effect could plausibly be produced if interchange reactions are more likely to occur at the more accessible chain ends of the branched macromolecule. This may be a reasonable assumption as there is some evidence that hyperbranched molecules do not entangle.[24] Interchange reactions between the methyl ester B groups are possible but do not result in a net change in the mass distribution; however, such a change can be produced by the interchange of a methyl ester end group in one polyester molecule with a main chain ester linkage in another. The molecule originally bearing the methyl ester is increased in mass as the ester end group is converted into a main chain ester, as shown in Figure 15. If the weight-average molecular weight is to increase, due to the reaction between a large hyperbranched polyester molecule and a smaller macromolecule, it must be the larger molecule that increases in size. The larger hyperbranched molecules have more methyl ester end groups, and hence this type of interchange favors the growth of the larger molecules and increases the weight-average molecular weight.

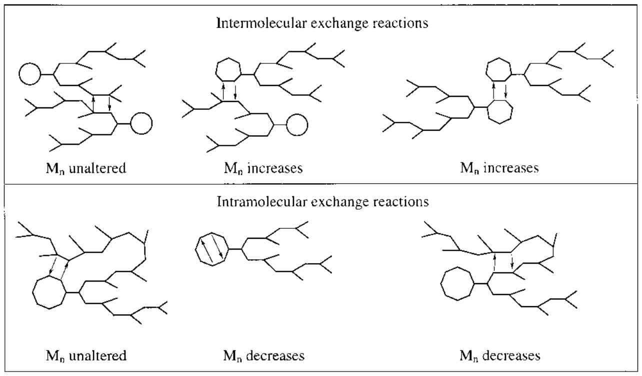


Figure 16. Schematic representation of the effect upon M_n of potential ester interchange reactions in a fully cyclized hyperbranched polyester.

Intermolecular interchange reactions do not affect the number-average molecular weight of a linear polymer as there is no net change in the number of molecules; however, the situation is much more complicated for a cyclized hyperbranched molecule. Both intermolecular and intramolecular reactions are possible and may involve the cyclized and/or the branched part of the molecule. The various possible interchange reactions have different effects upon M_n and are summarized in Figure 16. In general, intermolecular interchange reactions reduce the number of molecules present and

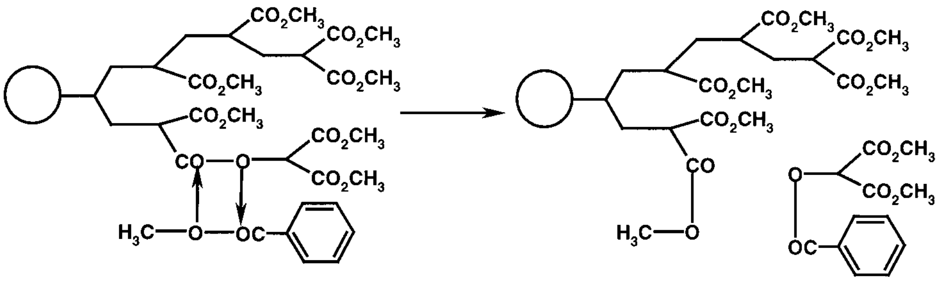


Figure 17. Schematic representation of possible interchange reactions between a fully cyclized polyester and a potential core molecule.

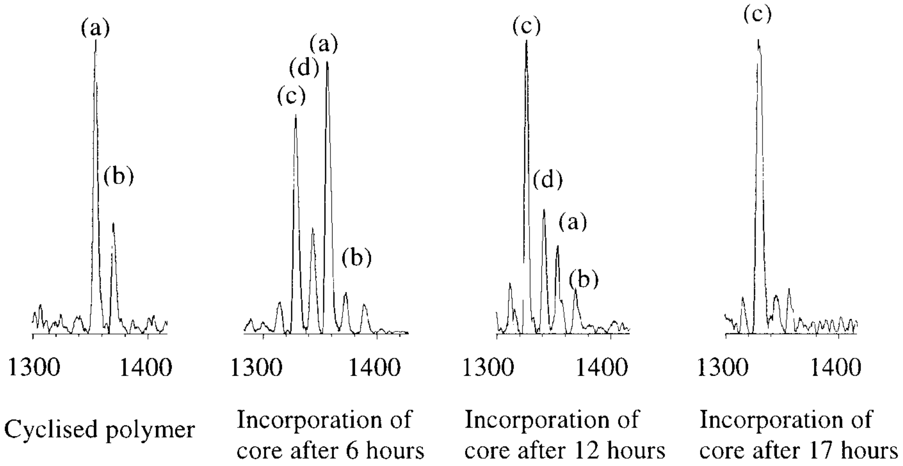
increase M_n; conversely, intramolecular interchange increases the number of molecules and decreases M_n. Exceptions are the intermolecular interchange reaction between the branched parts of two hyperbranched macromolecules and the intramolecular reaction between a cyclic and branched part of the same molecule, both of which have no effect upon M_n. If all these potential interchange reactions occur with equal probability, there would be no net change in the number-average molecular weight as there are an equal number of ways to increase M_n as there are to decrease it. However, this seems unlikely as interchange reactions involving a cycle are expected to be subject to greater steric constraints. This is particularly true if the cycle is small as is suggested by the MALDI-TOF MS results. If the most likely interchange reaction is an intermolecular reaction involving the methyl ester end groups, as was suggested in the discussion of M_w, the number of molecules remains the same and the number-average molecular weight is unaffected.

The above considerations have shown that the postulated occurrence of ester interchange reactions is consistent with the observed molecular weight growth behavior of these hyperbranched polyesters. This is also consistent with the shape of the molecular weight distribution as observed in SEC. A single distribution is expected to arise from random condensations in a step growth polymerization; however, the SEC traces obtained for the hyperbranched polyesters are polymodal. Presumably, if interchange reactions are favoring the growth of the larger molecules, then this would give rise to a further two distributions of large and small molecules as the larger molecules grow at the expense of the smaller ones.

Incorporation of a Core Molecule by Ester Interchange. A related study of core-terminated hyperbranched polyesters demonstrated that hyperbranched, cyclized, and core-terminated polymers could be distinguished by MALDI-TOF mass spectroscopy.[25] This suggested a method of exploring the possibility of ester exchange in these systems. It was postulated that if an AB_2 monomer were to undergo polycondensation until the point at which the resulting polymer was completely cyclized, then any further reaction would not be possible by a polycondensation mechanism. If at this point a potential core molecule (B_n) is introduced, then it is possible that the core molecule could be incorporated into the polymer by an ester exchange mechanism, as shown in Figure 17. Incorporation of the core is of course not possible by a simple condensation mechanism as there would be no available A groups for this type of reaction. Hence, the appearance of core-terminated species in the mass spectrum of a fully cyclized polymer, after reaction with a core molecule (B_n), would provide support for the hypothesis that ester exchange occurs in these systems.

Dimethyl 5-(2-hydroxyethoxy)isophthalate was polymerized in the melt, at 240 °C, sampling at frequent intervals. The polymerization was continued until the polymer was completely cyclized, as revealed by MALDI-TOF mass spectrometry. The polymer was ground up and combined with dimethyl isophthalate to give a 50/50 mixture (w/w), which was reheated, at 220 °C. The polymerization was sampled after 6, 12, and 17 h. The MALDI spectrum of the initial polymer sample, before the addition of the dimethyl isophthalate core, showed only the presence of cyclic polymer species. After 6 h heating signals corresponding to core-terminated polymer were evident and with a signal intensity comparable to that for the cyclic polymer species, as shown in Figure 18. The intensity of the signals due to core-terminated polymer increased with further heating, being the predominant species after 12 h and the sole species after 17 h. The complete dominance of core-terminated species, in the MALDI spectrum, is surprising but may be a result of using a high ratio of core molecule in the reaction.

Degree of Branching. The ^{13}C NMR spectra of the polymers revealed resolvable fine structure, exemplified in Figure 19, attributable to the various possible branching environments illustrated in Figure 20. Increased resolution was achieved by acquiring the spectrum at elevated temperature (100 °C) in tetrachloroethane-d_2. The signals were seen as partially resolved multiplets, which required a deconvolution procedure and integration to calculate the degree of branching. This procedure was carried out for three different polymer samples of low, intermediate, and high molecular weight (M_w = 9800, 37 900, and 136 200 PS equivalents, respectively). The component parts of a given multiplet were assigned on the basis of the relative line widths, which reflects the relative mobility of the different branching units. A given carbon atom within a branching unit might be expected to have less freedom of movement, and hence a shorter relaxation time leading to broader line widths, than the same carbon within a more mobile terminal unit. Thus, signals for carbons of fully branched units were expected to have the broadest line widths, terminal units the narrowest, and linear units to be intermediate between the two. Degrees of branching averaged for all carbon signals were 0.5, 0.6, and 0.5 ± 0.1 for the low, intermediate, and high molecular weight polymers, respectively. This is in reasonable agreement with the theoretical value for a statistical distribution at complete conversion (DB = 0.5), although the effects of redistributing branch units through transesterification might also be expected to tend toward statistical branching.



Cyclised polymer

Incorporation of core after 6 hours

Incorporation of core after 12 hours

Incorporation of core after 17 hours

Figure 18. Incorporation of dimethyl isophthalate into the fully cyclized hyperbranched polyester with time, as shown by MALDI TOF mass spectroscopy: (a) cyclic DP 6 $[M + Na]^+$; (b) cyclic DP 6 $[M + K]^+$; (c) DP 5 + core $[M + Na]^+$; (d) DP 5 + core $[M + K]^+$.

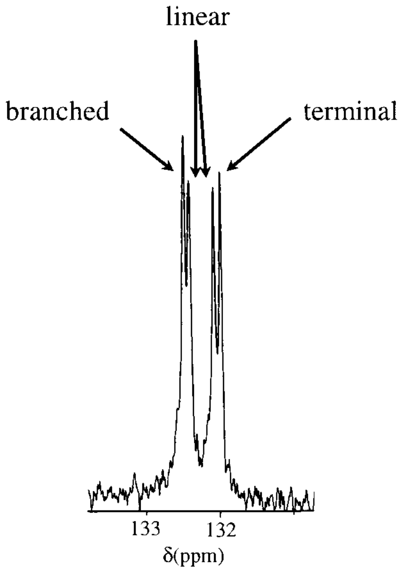


Figure 19. Expansion of ^{13}C NMR signal showing effect of branching. Only the signal due to the aromatic carbon adjacent to the carbonyl group is shown.

Thermal Properties. The AB_2 hyperbranched polyesters were analyzed by differential scanning calorimetry (DSC). All samples showed a single glass transition with no evidence of melting or crystallization peaks. This is consistent with the formation of an amorphous polymer. The lack of crystallinity is to be expected from these highly branched materials and has been observed for many other dendritic and hyperbranched polymers.[9,26] The glass temperature (T_g) varies from 73 to 86 °C and tends toward a limiting value of 86 °C as the molecular weight is increased, as shown in Figure 21. This tendency of the glass temperature to approach a limiting value is similar to the reported behavior of dendritic polyethers.[27] Stutz has argued that for dendritic polymers the glass temperature is dependent upon the end group conversion and the degree of branching, both of which approach a limiting value at high generation number.[28] A similar situation is expected for hyperbranched polymers where both the theoretical degree of branching and theoretical end group conversion can be shown to approach a finite limit with increasing degree of polymerization.

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 2, 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.[29]

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

This can be simplified to eq 3, where K is equal to $(2\theta\rho N_A/\alpha_f)$ and is a constant.

$$T_g = T_g^\infty - K/M_n \tag{3}$$

To examine whether this holds true for the hyperbranched polyesters, described in this study, the T_g data were plotted against the reciprocal molecular weight. This gave a good linear plot (correlation coefficient 0.98) as shown in Figure 22. Only the weight-average molecular weight was used in this analysis as the number-average molecular weight reaches an apparent maximum relatively early on in the polymerization. Fréchet has 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 4, where $K' = (\theta\rho N_A/\alpha_f)$ and η_e is the number of end groups, is more appropriate.

$$T_g = T_g^\infty - K'(\eta_e/M) \tag{4}$$

However, this does not take into account the fact that the number of end groups in a hyperbranched or dendritic polymer is determined by the degree of polymerization. Flory has shown that for an AB_2 polymer the number of unreacted B groups in a given x-mer is simply $(x + 1)$.[30] For an AB_2 addition polymerization, for example hyperbranched poly(amidoamines) prepared via Michael addition, the mass of an x-mer is xM_0, where M_0 is the monomer mass. Hence, the ratio of end groups to the polymer mass may be expressed in terms of the masses of polymer and monomer, eqs 5−7.

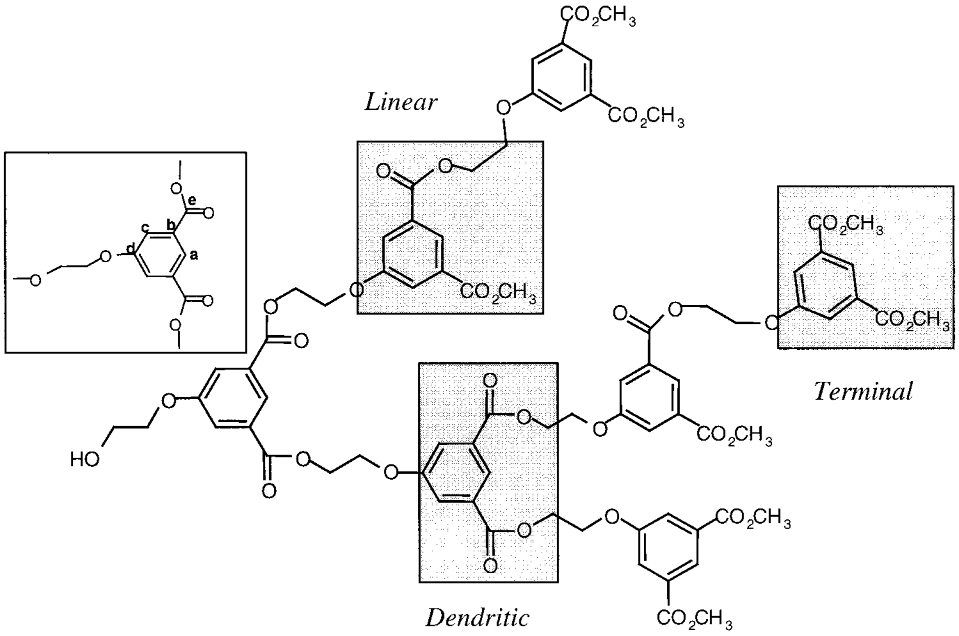


Figure 20. Branching environments in the hyperbranched polymer derived from dimethyl 5-(2-hydroxyethoxy)isophthalate. Only those carbons shown in the inset labeled a, b, c, and e exhibit effects due to branching.

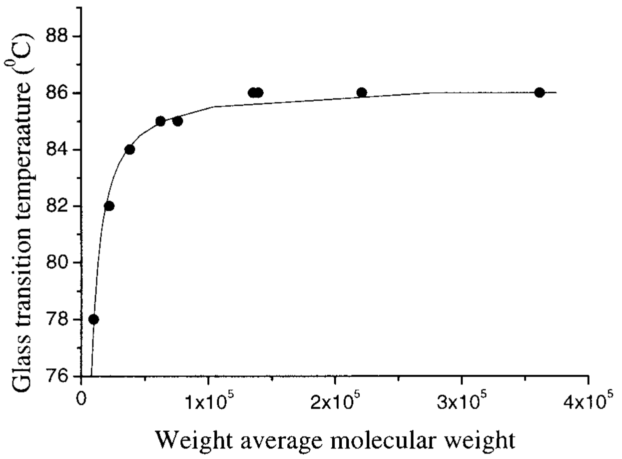


Figure 21. Variation of T_g with molecular weight for hyperbranched polyesters.

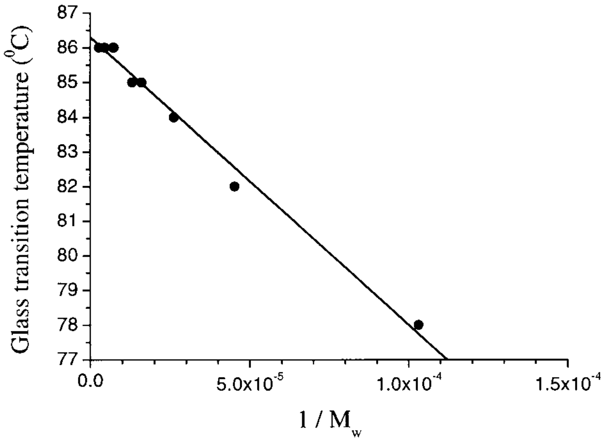
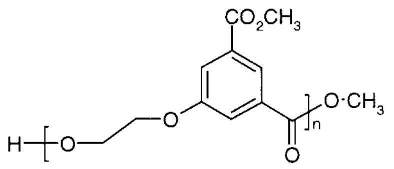


Figure 22. Variation of T_g with the reciprocal molecular weight for hyperbranched polyesters.



$$M = xM_r + M_c$$

Figure 23. Calculation of molecular weight for an AB_2 condensation polymer, where M_r is the mass of a repeat unit and M_c is the mass of a condensate molecule, in this example methanol.

number of end groups $= \eta_e = (x + 1)$

$$\frac{\eta_e}{M} = \frac{x+1}{M} \qquad (5)$$

substituting $x = M/M_0$, where M_0 is the monomer mass

$$\frac{\eta_e}{M} = \frac{M/M_0 + 1}{M} \qquad (6)$$

and so

$$\frac{\eta_e}{M} = \frac{1}{M_0} + \frac{1}{M} \qquad (7)$$

It is apparent from eq 7 that the ratio η_e/M is equal to $1/M$ plus a constant ($1/M_0$), and hence a plot of T_g vs $1/M$ might be expected to give linear relationship for AB_2 addition polymers. It can also be shown that for AB_2 condensation polymers η_e/M is again proportional to $1/M$. In this case, solely for the purposes of calculating the molecular weight, it is useful to consider the hyperbranched polymer as a number of repeat units linked together in a linear fashion, as shown in Figure 23. When the polymer is represented in this manner, it can clearly be seen that the molecular weight of an x-mer corresponds to the mass of x repeat units plus the mass of the chain end groups (i.e., the mass of a condensate molecule). Using this relationship between the polymer mass and the degree of polymerization, in Fréchet's expression for the number of chain ends, again leads to a linear relationship between η_e/M and $1/M$, eqs 8−10.

the number of end groups $= \eta_e = (x + 1)$

$$\frac{\eta_e}{M} = \frac{x+1}{M} \tag{8}$$

substituting $x = (M - M_c)/M_r$, where M_r is the mass of the repeat unit and M_c the mass of a condensate molecule

$$\frac{\eta_e}{M} = \frac{((M - M_c)/M_r) + 1}{M} \tag{9}$$

$$\frac{\eta_e}{M} = \frac{1}{M_r} + \frac{1}{M}\left(1 - \frac{M_c}{M_r}\right) \tag{10}$$

Thus, for the hyperbranched polyesters described in this work there is a linear relationship between η_e/M and $1/M$ which explains how it is possible to obtain a linear relationship between T_g and $1/M$ without taking account of the number of end groups. While the above considerations explain the linear dependence of T_g upon the reciprocal molecular weight, the fact that the glass temperature is dependent upon the reciprocal of the *weight-average* molecular weight has not been explained. In the treatment of linear polymers M_n is usually used, while Fréchet's modified treatment for dendrimers employs the molecular weight of a single dendrimer molecule. In a linear polymer the chain end free volume is dependent upon the number of molecules and hence simply related to the number-average molecular weight. However, in the case of a hyperbranched polymer the number of end groups, and hence the chain end free volume, depends upon not only the number of polymer molecules but also their degree of polymerization. Therefore, it seems reasonable to expect the chain end free volume to be related to the weight-average molecular weight.

Summary and Conclusions

Hyperbranched polyesters were prepared by simple condensation polymerization of the AB_2 monomer dimethyl 5-(2-hydroxyethoxy)isophthalate. The hyperbranched polyesters were statistically branched (DB = 0.5), as determined by quantitative ^{13}C NMR spectroscopy. 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. Unusual molecular weight growth characteristics were demonstrated. The number-average molecular weight (M_n) attained a maximum value after relatively short polymerization time, whereas the weight-average molecular weight (M_w) continued to increase. This limit to the attainable number-average molecular weight is thought to be a consequence of intramolecular cyclization reactions, contributing to the consumption of the remaining A groups. This effectively prevents further growth by a polycondensation mechanism. Evidence of cyclization in the hyperbranched polyesters was provided by MALDI-TOF MS. The weight-average molecular weight continues to increase after complete cyclization, and it is postulated that this is due to a redistribution of polymer chains by ester interchange reactions. It is conjectured that interchange reactions are more likely to occur at the more accessible chain ends of the branched macromolecule, possibly involving reaction of the methyl ester end groups. The larger hyperbranched molecules have more methyl ester end groups, and hence this type of interchange favors the growth of the larger molecules. The plausibility of the occurrence of ester exchange processes was demonstrated by the successful incorporation of dimethyl isophthalate into a fully cyclized hyperbranched polyester. The molecular weight growth behavior reported here has not been observed for other hyperbranched polymers. The presence of cyclization and the consequent restriction of polymer growth have been observed in other systems, but the continued increase in weight-average molecular weight appears to be unique to the polymerization of dimethyl 5-(2-hydroxyethoxy)isophthalate.

Acknowledgment. We thank the EPSRC for a grant to the IRC and Dr. Alan Kenwright for NMR measurements.

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dominant cycle to be a trimer. This is erroneous; trimers are excluded from our analysis, and there is no firm evidence pertaining to either cycle size or the most predominant cyclic species.

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MA0018805