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The synthesis and characterisation of hyperbranched poly(diethyl 3-hydroxyglutarate)

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Hyperbranched aliphatic polyesters derived from the AB_2 monomer diethyl 3-hydroxyglutarate in the presence of titanium(IV) butoxide are reported. The oligomeric products were characterised by GPC, NMR spectroscopy and MALDI-TOF mass spectrometry. The degree of branching, molecular weights and the possibility of intramolecular cyclisation reactions have been evaluated. MALDI-TOF mass spectrometry was used to quantify the extent of possible side reactions, particularly those resulting from alkoxide exchange with the catalyst.

The field of hyperbranched and dendritic polymers is of interest chiefly because of the unusual properties associated with these macromolecular architectures.[1–3] These materials, whether perfectly regular monodisperse dendrimers,[4,5] or the less well defined hyperbranched structures,[6] possess a large number of branches and hence numerous end groups. Consequently, physical properties which contrast with those of conventional linear polymers are to be expected. Indeed, the recent literature includes a number of articles contrasting the physical properties of linear, dendritic and hyperbranched polymers constructed from analogous units.[7,8] From these and related studies[9] it can be concluded that thermal properties are largely independent of architecture but extremely sensitive to both the number and nature of the end groups; whilst solubility, viscosity and reactivity are heavily influenced by topology.

Since Kim and Webster reported the first synthetic hyperbranched polymer,[10] work in this field has shown that materials which retain many of the structural features and physical properties of monodisperse dendrimers can be prepared at a lower cost *via* the single step polymerisation of an AB_x ($x > 1$) monomer. For example, the intrinsic viscosity–molecular weight relationship, which has been shown to pass through a maximum for dendrimers[11] and described as one of their characteristic features, has also been established for a core terminated hyperbranched polymer with a high degree of branching.[12]

Although a number of different routes to hyperbranched polymers have been reported, including the use of self-condensing vinyl polymerisation[13] (SCVP) and atom transfer radical polymerisation[14] (ATRP) techniques, simple poly-condensation reactions are the most common. Following Kricheldorf's synthesis of hyperbranched polyesters, from mixtures of 3-(trimethylsiloxy)benzoyl chloride and 3,5-bis(trimethylsiloxy)benzoyl chloride,[15] a series of publications have addressed key analytical problems; namely, calculation of degree of branching,[16,17] the possibility of intramolecular cyclisation[18–20] and the inherent problems associated with molecular weight determination for non-linear structures.

Experimental section

Materials and methods

All organic reagents were purchased from the Aldrich Chemical Company and used as received without further purification. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR. ^1H and ^{13}C NMR spectra were recorded using a Varian 400 MHz spectrometer. DSC measurements were recorded using a Perkin-Elmer DSC7, at a scanning rate of 10 °C min^{-1}. GPC was performed using a Waters system with a differential refractometer detector and three PL-gel columns (exclusion limits 100, 10^3 and 10^5 Å) with $CHCl_3$ as the eluent. Columns were calibrated using polystyrene standards (Polymer Labs). Solution viscosity measurements were carried out in chloroform, at 25 °C over a range of dilutions, using a Laude/Schott automated system. MALDI-TOF mass spectra were recorded using the Kratos Kompact MALDI IV instrument (nitrogen laser 337 nm) operated in both linear and reflection mode to generate positive ion spectra. The MALDI-TOF spectra reported were calibrated against a range of external standards. Samples were prepared for analysis by MALDI-TOF MS by first laying down the matrix solution, 0.5 µl of a 10^{-1} mol dm^{-3} solution of 2,5-dihydroxybenzoic acid in water–acetonitrile (40:60), followed by 0.5 µl of a 10^{-3} mol dm^{-3} polymer solution in acetone.

Polymerisation procedures

The general procedures adopted are illustrated by specific examples.

Method (*a*). Titanium(IV) butoxide (0.1 g, 0.29 mmol) was added to a glass reaction vessel fitted with a mechanical stirrer and containing diethyl 3-hydroxyglutarate (2.0 g, 9.80 mmol). The reactor was immersed in a preheated oil bath, held at 80 °C, and the temperature raised to 100–125 °C at a rate of *ca.* 3 °C min^{-1}. The reaction vessel was maintained at this temperature for 3.5–6.5 h with stirring, a vacuum (10 mmHg) being applied during the final 30 min. The product, a viscous yellow liquid, was dissolved in chloroform (300 ml) and washed with water (3 × 200 ml) to remove the catalyst. The organic fraction was separated and concentrated under reduced pressure to yield the hyperbranched polymeric product as a pale-yellow oil.

Method (*b*). Titanium(IV) butoxide (50 mg, 0.147 mmol, 1.0 wt%) was added to a glass reaction vessel fitted with a mechanical stirrer and containing diethyl 3-hydroxyglutarate (5.0 g, 24.48 mmol). The reactor was heated to 170 °C at a rate of 10 °C min^{-1} and maintained at this temperature for 2.0–4.0 h with stirring. After cooling under nitrogen, the hyperbranched

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polymer was isolated from the reaction flask and characterised without further purification.

Results and Discussion

As part of an ongoing research programme into the preparation of hyperbranched polyesters, we report here the synthesis of a series of aliphatic hyperbranched polyesters from the commercially available AB_2 monomer, diethyl 3-hydroxyglutarate, *via* a titanium(IV) butoxide catalysed step-growth condensation process. The synthesis, polymerisation and characterisation of a series of dimethyl 5-(hydroxyalkoxy)isophthalates has previously been described[20] but this new system represents one of the few examples of completely aliphatic hyperbranched polyesters, the only prior examples being described by the group of Hult.[21]

Diethyl 3-hydroxyglutarate was polymerised in the bulk at elevated temperatures and a systematic variation of catalyst concentration, reaction time and temperature was undertaken in an attempt to optimise the polymerisation. Initial reactions were carried out using method (*a*) (see Experimental section) and it was observed that although polyesterifications are usually performed in the presence of 0.05–0.5 wt% titanium alkoxide catalysts,[22] for this system studies showed that when the reaction time and temperature were kept constant at 270 min and 100 °C respectively, 5.0 wt% of catalyst relative to the monomer appeared to be optimum.[23] However, even at such high catalyst concentrations, polymerisations failed to give high molecular weight products as have been observed for other AB_2 hyperbranched polyesters studied.[20] Other catalysts, including the manganese acetate–antimony trioxide system used in the synthesis of PET, were investigated but no substantial molecular weight improvements were observed. It is also noteworthy that after prolonged heating (210 °C, 4 h) in the absence of a catalyst, less than 2% polymerisation and no degradation products were observed. While in the presence of 2–5 wt% of titanium butoxide catalyst variation of reaction temperature across the range 100–170 °C also produced no significant molecular weight improvement. This was an unexpected result which merited investigation and explanation.

Structural characterisation

The materials prepared were characterised by a combination of analytical techniques, including NMR and IR spectroscopy, DSC, GPC and MALDI-TOF mass spectrometry.

Using ^1H (Fig. 1) and ^{13}C (Fig. 2) NMR spectroscopy it could be shown that polymerisation occurred through reaction of the alcohol (A group) and ethyl ester (B group) functionalities of the AB_2 monomer. The ^1H NMR spectrum of the polymer shows a major triplet at 1.26 ppm (*a*) due to the CH_3 hydrogens of the terminal ester units, whilst the multiplet at 4.15 ppm (*b*) is due to the OCH_2 hydrogens of the ethyl groups. The minor multiplet at 2.54 ppm (*d*) coincides in chemical shift with the CH_2 doublet of the monomer, and can therefore be assigned to the CH_2 hydrogens adjacent to the polymer foci whereas the major signal at 2.69 ppm (*e*) is assigned to the analogous CH_2 hydrogens in the branched, linear or terminal sub-units of the polymer. The minor multiplet at 4.44 ppm (*f*) is due to the $CH{-}OH$ hydrogen of the focus, whilst the signal at 5.51 ppm (*g*) is due to $CH{-}O{-}CO$ of a methine hydrogen in the branched, linear or terminal sub-units of the polymer.

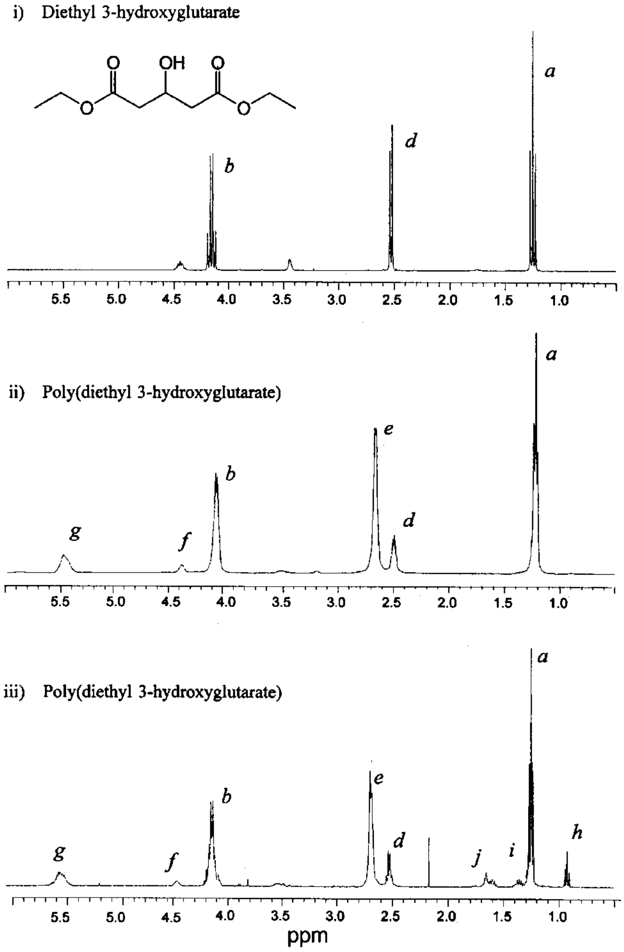


Fig. 1 ^1H NMR spectroscopy data: i) diethyl 3-hydroxyglutarate monomer, ii) poly(diethyl 3-hydroxyglutarate) prepared by method (*b*) using 0.5 wt% titanium butoxide catalyst at 170 °C, 4.0 h, $M_n \sim 1400$ (^1H NMR data), iii) poly(diethyl 3-hydroxyglutarate) prepared by method (*a*) using 5.0 wt% titanium butoxide catalyst at 100 °C, 3.5 h, $M_n \sim 800$ (^1H NMR data)

As, in the ideal case considered by Flory,[24] every polymer wedge has a single A group at its focus, ^1H NMR spectroscopy also allows calculation of an idealised number average degree of polymerisation, extent of reaction and number average molecular weight. These calculations rely upon the premise that there are no intramolecular cyclisation reactions between the focal point and the terminal groups, as this would result in an overestimation of M_n by such end group counting techniques. For these polyesters such calculations were carried out on the basis of the integrated intensities of the signal at 4.44 ppm (*f*), assigned to the $CH{-}OH$ of the focal point and that of the $CH{-}O$ signal at 5.51 ppm (*g*) assigned to the combined linear, terminal and branched sub-units. An analogous pair of signals are those due to the CH_2 at 2.54 (*d*), the focus, and 2.69 (*e*) ppm, the combined linear, terminal and branched sub-units.

In the ^{13}C NMR spectrum the signal observed at 14.14 ppm (*a*) is assigned to the CH_3 of the terminal esters, whilst the signal at 60.82 ppm (*b*) arises from the OCH_2 of the ethyl groups. The minor peak at 40.61 ppm (*d*) is due to the CH_2 of the focal units whilst the signal at 38.23 ppm (*e*) is due to the CH_2 of the remaining linear, terminal and branched sub-units; in theory, this latter signal could be deconvoluted to determine the degree of branching, however, the peak at 67.19 ppm (*f*), due to the combined $CH{-}O{-}$ signals for linear, branched and terminal units was better resolved making the assignment and relative intensity measurement of the constituent signals simple and straightforward. The $CH{-}OH$ of the focus is distinct and readily observable at 64.73 ppm (*f*). The carbonyl region of the spectrum (*c*) shows a number of peaks, consistent with several carbonyl environments, as expected.

As described, quantitative ^{13}C NMR spectroscopy provides a method to calculate the degree of branching (DB), a parameter that has received much attention of late; Frey's re-

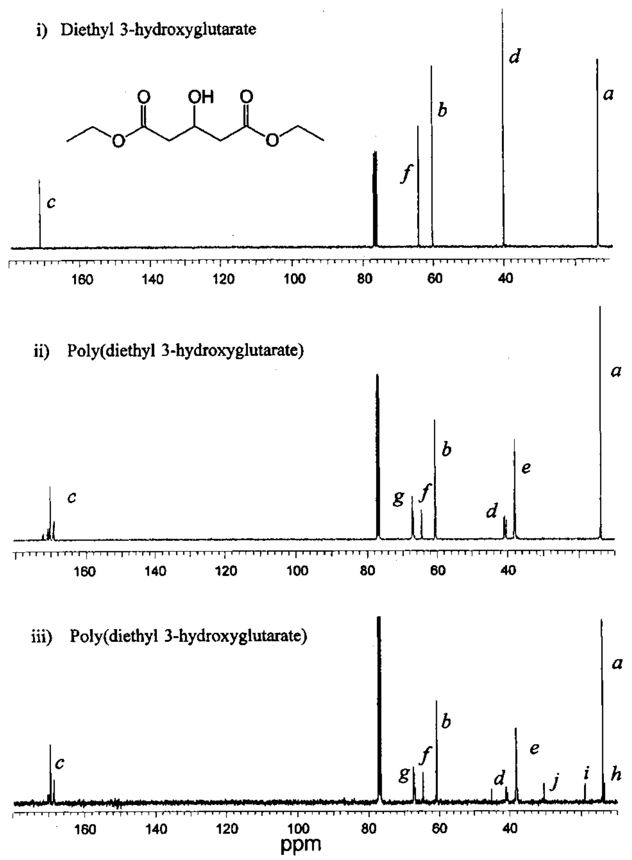
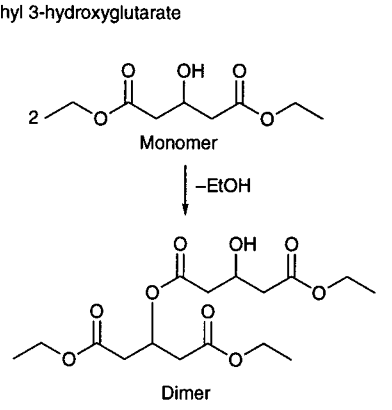


Fig. 2 ^{13}C NMR spectroscopy data: i) diethyl 3-hydroxyglutarate monomer, ii) poly(diethyl 3-hydroxyglutarate) prepared by method (*b*) using 0.5 wt% titanium butoxide catalyst at 170 °C, 4.0 h, $M_n \sim 1400$ (^{1}H NMR), iii) poly(diethyl 3-hydroxyglutarate) prepared by method (*a*) using 5.0 wt% titanium butoxide catalyst at 100 °C, 3.5 h, $M_n = 800$ (^{1}H NMR data). (The signal observed at 45 ppm has been confirmed as a machine artefact related to that at ~150 ppm.)

evaluation of the definition of DB[17] receiving broad acceptance in the field. Calculation of DB for the polyesters prepared in this study gives values between 0.52 and 0.57 (±0.05), consistent with a statistically branched structure as proposed by Flory for an AB_2 system in the absence of cyclisation.

During a typical step growth condensation polymerisation one molecule is eliminated at each step; the first step in the polymerisation of diethyl 3-hydroxyglutarate is shown in Scheme 1.



Scheme 1 First step in the step growth polymerisation of diethyl 3-hydroxyglutarate

Thus, it is expected that the polymerisation process will give rise to a series of peaks in the mass spectrum which may be represented as:

$$Y = nM - (n-1)\mathrm{EtOH} + x \quad Y = n(M - \mathrm{EtOH}) + 46 + 23$$

$$\text{therefore } n = \frac{Y - 69}{158}$$

Where Y is the observed peak mass from the spectrum, n is the number of monomer units incorporated, M is the monomer molecular mass (204), 46 is the molecular mass of the eliminated ethanol and x is the molecular mass of the associated cation, sodium in the example above.

Analysis of the MALDI-TOF spectrum obtained from a sample of poly(diethyl 3-hydroxyglutarate) prepared by method (*b*), using 0.5 wt% titanium butoxide catalyst, revealed a main series of peaks corresponding to the predicted oligomers detected as the sodium cation attached species, Fig. 3. Peaks corresponding to DP 2–18 were well resolved and therefore easily assigned. The minor series, located at major series peak masses plus 16 amu, can be assigned as the corresponding potassium cation attached species.

When larger quantities of the titanium butoxide catalyst were used, namely 2.5, 5, 10 and 25 wt% [method (*a*)], additional signals were present in both the ^{1}H and ^{13}C NMR spectra. The minor multiplets arising in the ^{1}H NMR spectrum (Fig. 1 iii) at 0.93 (*h*), 1.36 (*i*), and 1.60 ppm (*j*) and represented in the ^{13}C NMR spectrum, (Fig. 2 iii) at 13.68 (*h*), 19.06 (*i*) and 30.51 ppm (*j*), can be assigned to the methyl and two methylene units of a butoxide residue arising from exchange with the catalyst. Analysis of these samples by MALDI-TOF MS confirms the suspected ethoxide–butoxide exchange. The spectra reveal additional discrete series of peaks associated with each oligomer, corresponding to exchange of one or multiple ester ethoxides by butoxide groups from the catalyst; Fig. 4 shows a typical example.

This is shown more clearly in the expansion of the spectrum between *m*/*z* 1480 and 1750, Fig. 5, where ethoxide–butoxide exchange at DP 9 and 10 is illustrated.

These subsequent series can be described by the following equation, where α represents the number of butoxide groups exchanged per molecule.

$$Y = nM - (n-1)\mathrm{EtOH} + x + (C_2H_4)\alpha$$

From the MALDI-TOF spectrum reproduced as Fig. 4, we observe that the relative proportion and number of species detected showing butoxide exchange increases as we go to higher molecular weight. This is expected because butoxide exchange can only occur at the ester end groups and, by the very nature of an AB_2 polymerisation, at higher DP there are more end groups per molecule and therefore it is statistically more likely that butoxide exchange will occur. The MALDI-

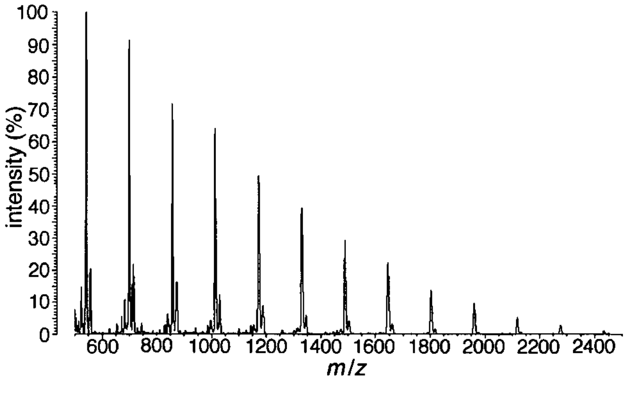


Fig. 3 MALDI-TOF spectrum of poly(diethyl 3-hydroxyglutarate) prepared by method (*b*), 170 °C, 4 h, using 0.5 wt% titanium butoxide catalyst

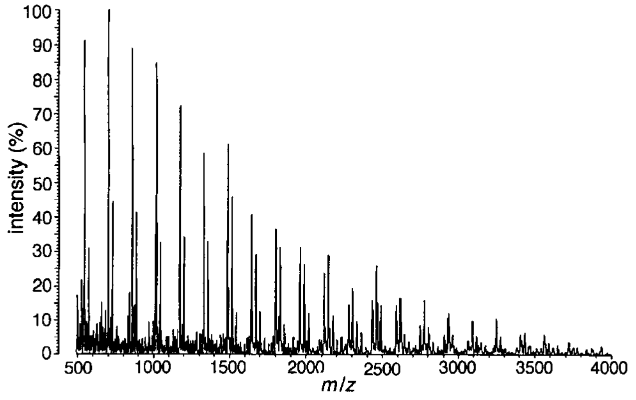


Fig. 4 MALDI-TOF spectrum of poly(diethyl 3-hydroxyglutarate) prepared using 5 wt% catalyst, method (*a*), 100 °C, 3.5 h

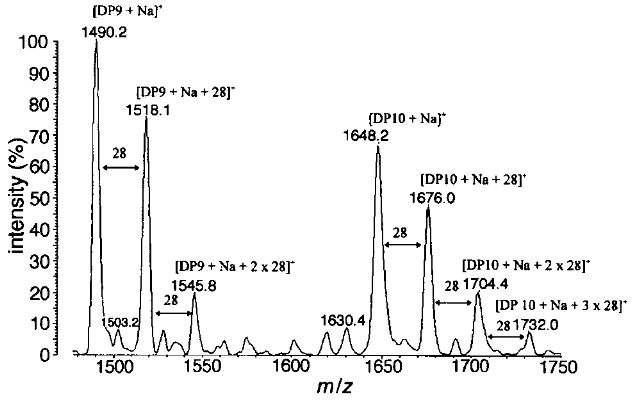


Fig. 5 Expansion of MALDI-TOF spectrum of poly(diethyl glutarate), reproduced as Fig. 4, to illustrate ethoxide–butoxide exchange

TOF spectra reproduced as Fig. 3–5 were generated using the Kratos Kompact MALDI IV spectrometer operated in linear detection mode, to generate positive ion spectra. The same information was obtained using the instrument in reflection mode.

From the NMR studies undertaken it is possible to calculate percentage butoxide exchange as a function of both temperature and the initial wt% of titanium butoxide catalyst added to the polymerisation mixture.

The results, Table 1, show a general trend towards increasing extent of butoxide exchange with temperature across the limited range studied. On inspection of the ^{1}H NMR spectra of the polymers produced in the presence of 2.5, 5, 10 and 25 wt% catalyst, it was clear that the concentration of butoxide groups present in the polymer increased as the amount of catalyst used increased, Table 2. It was possible to determine the amount of butoxide exchange present in the polymer from the relative integrated intensities of the ethyl triplet at 1.26 ppm (*a*) and the butoxide CH_3 triplet at 0.93 ppm (*h*) since these signals are reasonably well resolved (Fig. 1 iii).

Neither NMR spectroscopy nor MALDI-TOF MS techniques provide any evidence to suggest the occurrence of side reactions, namely dehydration and intramolecular cyclisation between the focal OH group and the terminal ethyl ester groups. These would be the most likely reactions to compete with the polyesterification of diethyl 3-hydroxyglutarate, both of which would severely hinder polymerisation by removing the reactive hydroxy A group from the reaction. However, neither of these processes, distinguishable by MALDI-TOF MS through the observation of peaks at 18 and 46 amu less than the main oligomer peaks, were found to occur in these systems under any conditions. The failure to detect evidence for cyclic structures in the polymerisation product of diethyl 3-hydroxyglutarate is consistent with the results of Hawker and Chu for the polymerisation of 4,4-bis(4′-hydroxyphenyl) pentanoate ester[19] but in contrast to the work of Percec[18] and Feast[20] where cyclisation is shown to dominate in the polyesters studied. It can therefore be concluded that cyclisation is extremely system specific, even within the single class of hyperbranched polymers considered. It is possible that the probability of intramolecular cyclisation is related to the conformational mobility of the particular system.

Table 1 Characteristics of oligomers produced at 5 wt% catalyst concentration in 4.5 h reactions at different temperatures, using method (*a*)

T/°C	M_n[a]	BuO[b] (%)	DB[c] (±0.05)
100	2700	6.8	0.54
115	2200	7.3	0.57
125	2000	7.9	0.57

[a]As determined using GPC with $CHCl_3$ as eluent and linear polystyrene standards. [b]mol% of butyl ester groups. [c]As determined *via* ^{13}C NMR spectroscopy.

Molecular weight determination

In recent years, problems associated with molecular weight determination for non-linear polymers with a broad distribution of mass and structure have been highlighted. It is now widely accepted that there is no universally applicable ideal technique for such characterisations. Although MALDI-TOF MS allows some valuable assignment of the structural subunits of the polymer, which can provide useful insights into the mechanistic details of the polymerisation process and side reaction (*vide supra*), it is well documented that the technique fails to provide a realistic interpretation of either molecular weight or molecular weight distribution for materials with a wide polydispersity,[25,26] a classification which includes the hyperbranched polymers.[27] The spectrum, reproduced as Fig. 3, is of a low molecular weight sample of the polymer detected

Table 2 Characteristics of oligomers produced from 4.5 h reactions at 100 °C with varying amounts of catalyst, using method (*a*)

initial amount catalyst (wt%)	M_n[a]	BuO[b] (%)	DB[c] (±0.05)
2.5	820	5.1	0.44
5	2700	6.8	0.54
10	1800	15.1	0.52
25	1100	51.9	0.53

[a]As determined using GPC with $CHCl_3$ as eluent and linear polystyrene standards. [b]mol% of butyl ester groups. [c]As determined *via* ^{13}C NMR spectroscopy.

Table 3 Molecular weights of oligomers measured by GPC (M_n, M_w and PDI) and ^{1}H NMR spectroscopy (M_n)

GPC data ($CDCl_3$)			^{1}H NMR data ($CDCl_3$)	
M_n	M_w	PDI	M_n[a]	M_n[b]
3200	5000	1.58	2000	2100
2700	3800	1.38	2400	2600
2200	3200	1.45	1500	1800
2000	2700	1.35	1200	1600
2000	3100	1.52	1700	2100
1800	2400	1.33	870	990
1500	1900	1.24	760	850
1500	1900	1.28	970	1200
1100	1200	1.13	470	470
1100	1400	1.31	630	680
820	926	1.13	420	440

[a]Calculated from the aliphatic CH_2 region of the ^{1}H NMR spectrum. [b]Calculated from the CHO— region of the ^{1}H NMR spectrum.

as its sodium adduct. It has been proposed that by selective cationisation polymer spectra can be biased towards detecting the higher molecular weight species in the distribution, specifically, use of caesium and rubidium has been reported.[28] However in-depth analysis of these polyesters by MALDI-TOF MS, using the series of counter ions Li, Na, K, Rb and Cs, revealed no really significant change in the intensity distribution across the molecular weight range observed. Significantly, use of sodium as the counter ion gave the simplest spectrum over the widest range, as in the case of larger ions incomplete cationisation was observed over a range of solution concentrations. In the light of these observations and recent literature observations on the uncertainty of molecular weight measurement by this technique, we limited our use of MALDI-TOF MS to structural analysis in this study.

Although the problems associated with determining molecular weights of non-linear polymers by GPC are recognised, M_n, M_w and polydispersity indices are quoted for this system in terms of polystyrene equivalents, Table 3. These results are supported by comparison with the M_n values calculated from the corresponding ^{1}H NMR spectra by end group counting. Some reliability can be associated with these latter figures as MALDI-TOF MS has unequivocally shown that intramolecular cyclisation reactions do not occur for this system; in general it appears that the GPC analysis errs on the side of optimism.

Physical properties

The products of these polymerisations were oils; DSC experiments revealed T_g values in the range -35 to -65 °C. Although it is common practise to analyse these data in terms of observed T_g as a function of molecular weight, in this case the extent of reaction is too low and the molecular weight range too narrow to extract a meaningful relationship. Similarly, useful conclusions could not be drawn from intrinsic viscosity (η) measurements; η values for the polymers produced were in the range 1.00–5.00 cm^3 g^{-1}.

Conclusions

In summary, although AB$_2$ hyperbranched polyesters have been synthesised from diethyl 3-hydroxyglutarate in the presence of a titanium(IV) butoxide catalyst, the system fails to attain the high molecular weights reported for other hyperbranched polyesters. The observation that the monomer fails to react at elevated temperatures leads us to believe that, despite the similarity of the polymeric backbone to that of the systems described by Hult *et al.*, polymerisation will remain unfavourable whatever reaction conditions are employed.

However, the oligomeric materials produced were amenable to fairly detailed analysis, which provided insights into this polyesterification reaction. In particular MALDI-TOF MS has been shown to provide useful structural analysis of these relatively low molecular weight polyesters, revealing the absence of cyclic and dehydration by-products and allowing the identification of alkoxide exchange reactions during polymerisation. This exchange reaction between alkoxide ligands on the titanium catalyst and the alkoxide fragment of the terminal ester units in the hyperbranched polyester is, in this particular system, competitive with polymerisation. This feature, along with the steric shielding of the secondary alcohol focal unit, may account for the limited molecular weights attainable as compared with the superficially similar system studied by Hult.

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References

1 D. A. Tomalia, D. M. Hedstrand and L. R. Wilson, *Encyclopaedia of Polymer Science and Engineering*, Wiley, Chichester, 1990, 2nd edn., Index vol., p.46.

2 J. M. J. Fréchet and C. J. Hawker, *Comprehensive Polymer Science,* 2nd suppl., ed. S. L. Agarawal and S. Russo, Pergamon, Oxford, 1996, ch. 3.

3 L. J. Hobson and R. M. Harrison, *Curr. Opin. Solid State Mater. Chem.*, 1997, **2**(6), 683.

4 C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1990, **112**, 7638.

5 E. M. M. de Brabander-van den berg, A. Nijenhuis, M. Mure, J. Keulen, R. Reintjens, F. Vandenbooren, B. Bosman, R. Denaat, T. Frijins, S. V. D. Wal, M. Castelijns, J. Put and E. W. Meijer, *Macromol. Symp.*, 1994, **77**, 51.

6 A. Hult and E. Malmström, *J. M. S. -Rev. Macromol. Chem. Phys. C*, 1997, **37**, 555.

7 C. J. Hawker and J. M. J. Fréchet, *Am. Chem. Soc. Symp.*, 1996, **624**, 132.

8 C. J. Hawker, E. Malmström, C. W. Frank, J. P. Kampf, C. Mio and J. Prausnitz, *Proc. Am. Chem. Soc., Div. Polym. Mater.: Sci. Eng., Las Vegas*, 1997, **77**, 61.

9 E. Malmström, A. Hult, U. W. Gedde, F. Liu and R. H. Boyd, *Polymer*, 1997, **38**(19), 4873.

10 Y. H. Kim and O. W. Webster, *J. Am. Chem. Soc.*, 1980, **112**, 4592.

11 H. Mourey, S. R. Turner, M. Rubinstein, J. M. J. Fréchet, C. J. Hawker and K. L. Wooley, *Macromolecules*, 1992, **25**, 2401.

12 L. J. Hobson and W. J. Feast, *Chem. Commun.*, 1997, 2067.

13 J. M. J. Fréchet, M. Hemni, I. Gitsov, S. Aoshima, M. Leduc and R. B. Grubbs, *Science*, 1995, **269**, 1080.

14 S. G. Gaynor, S. Edelman and K. Matyjaszewski, *Macromolecules*, 1996, **29**, 1079.

15 H. R. Kricheldorf, Q-Z. Zhang and G. Schwarz, *Polymer*, 1982, **23**, 1821.

16 C. J. Hawker, R. Lee and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1991, **113**, 4583.

17 D. Holter and H. Frey, *Acta Polymerica*, 1997, **48**, 30.

18 V. Percec, P. Chu and M. Kawasumi, *Macromolecules*, 1994, **27**, 4441.

19 F. Chu, C. J. Hawker, P. J. Pomery and D. J. T. Hill, *J. Poly. Sci. Part A, Polym. Chem.*, 1997, **35**, 1627.

20 W. J. Feast, A. J. Keeney, A. M. Kenwright and D. Parker, *Chem. Commun.*, 1997, 1749.

21 E. Malmström and A. Hult, *Macromolecules*, 1995, **28**, 1698.

22 *Comprehensive Polymer Science, vol. 5: Step Polymerization*, ed. G. C. Eastmond, A. Ledwith, A. Russo and P. Sigwalt, Pergamon Oxford, 1989, ch. 17.

23 L. M. Hamilton, PhD Thesis, University of Durham, 1996.

24 P. J. Flory, *J. Am. Chem. Soc.*, 1952, **74**, 2718.

25 K. Martin, J. Spickermann, H. J. Rader and K. Mullen, *Rapid Commun. Mass Spectrom.*, 1996, **10**, 1471.

26 C. Jackson, B. Larson and C. McEwan, *Anal. Chem.*, 1996, **68**, 1303.

27 L. J. Hobson, A. M. Kenwright and W. J. Feast, *Chem. Commun.*, 1997, 1877.

28 A. T. Jackson, H. T. Yates, W. A. MacDonald, J. H. Scrivens, G. Critchley, J. Brown, M. J. Deery, K. R. Jennings and C. Brookes, *J. Am. Soc. Mass Spectrom.*, 1997, **8**, 132.

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