Synthesis, structure and cyclics content of hyperbranched polyesters

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Dimethyl 5-(hydroxyalkoxy)isophthalates undergo step growth condensation polymerisation to produce hyper-branched polymers with a degree of branching lower than statistically expected and with a high proportion of cyclic structures.

The step-growth condensation polymerisation of AB_x type monomers was described in a theoretical treatment by Flory, who predicted the formation of polydisperse polymers containing branched and linear segments.[1] It is often assumed that steric constraints preclude intramolecular reactions such as cyclisation, the absence of which is believed to be necessary for continued growth.[2,3]

Previously we have reported the single-step melt condensation polymerisation of dimethyl 5-(2-hydroxyethoxy)isophthalate.[4] As part of this continuing programme into the synthesis and properties of AB_x hyperbranched polymers we have studied the step growth polymerisation of a series of dimethyl 5-(hydroxyalkoxy)isophthalates.

HO(CH$_2$)$_n$—O—[benzene ring]—CO$_2$Me (top), CO$_2$Me (bottom)

n = 2–6
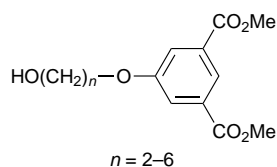
These AB_2 monomers underwent step growth polymerisation, eliminating methanol, on heating between 210 and 240 °C in a stream of dry nitrogen and in the presence of a transesterification catalyst which has found previous application in the commercial synthesis of linear polyesters. It utilises a combination of manganese(II) acetate and antimony trioxide, with triphenyl phosphate as a suppressor of thermal degradation.[5] The resulting AB_2 polyesters, unlike their linear analogues, were highly soluble in common organic solvents such as CHCl$_3$ and THF which allowed the determination of polystyrene equivalent molecular weights by size exclusion chromatography.

Variation of the alkylene chain length (*n* = 2 to 6) had a marked effect upon the polymerisation characteristics. When *n* = 2 both the molecular weight and polydispersity (M_w/M_n) of the polymer increased with increasing reaction time up to a weight average molecular weight of 107 000 and M_w/M_n values of 15 after 24 h. This continuous increase in M_w/M_n was as expected from Flory's predictions and has been observed in other hyperbranched systems.[6] However, on increasing the alkylene chain length (*n* = 3 to 6) this steady increase in molecular weight and polydispersity with reaction conversion was no longer observed. The molecular weight in these instances was found to increase until a maximum was reached, after which it remained constant and no further growth was apparent. This phenomenon is consistent with deactivation or loss of the A functionality. Furthermore an 'odd/even effect' was observed, with alkylene chain lengths of 2, 4 and 6 methylene units yielding higher molecular weights than the corresponding 3 and 5 methylene chain polymers.

Copolymerisation of the AB_2 monomer, where *n* = 2, with potential B_2 (dimethyl isophthalate) and B_3 (trimethyl benzene-1,3,5-tricarboxylate) core molecules afforded a method of molecular weight control for these systems. Increasing the core to monomer ratio resulted in a decrease in molecular weight and a narrowing of the polydispersity. In principle, an AB_2 condensation polymerisation can give rise to branched linear or terminal units (Fig. 1). A measure of the relative proportions of these structural units, the degree of branching (DB), is defined in eqn. (1), where N_x is the number of type x units in the structure.

$$DB = \frac{N_b + N_t}{N_b + N_l + N_t} \qquad (1)$$

Quantitative ^{13}C NMR spectra of the polymers with *n* = 2 at elevated temperature reveals fine structure attributable to the different types of repeat units in the polymers. These may be assigned to branched, linear and terminal contributions on the basis of their line-widths; the branched species are expected to be the least mobile and hence have the wider line-width, whilst the more mobile terminal species will have the narrower linewidth. Analysis of the ^{13}C NMR signals from the ester carbons (Fig. 2) gave a degree of branching of *ca* 0.5 which was independent of molecular weight. Analysis of the aromatic carbons in the structure confirm this DB. Purely statistical polymerisation would give a value of 0.66.

MALDI-TOF mass spectrometry (2,5-dihydroxybenzoic acid matrix + KCl, Kratos Kompact MALDI IV, linear mode) of polymers where *n* = 2 or 3 showed a series of peaks corresponding to degrees of polymerisation in the range 3 to 16 (Figs. 3 and 4, for *n* = 2). Ions were observed as their [M + K]$^+$ species. For low molecular weight polymers the main ion series corresponds to oligomers resulting from 3 to 16 simple condensation steps where the mass of an oligomer of *n* units is [*n* × (monomer mass) − (*n* − 1) × (mass of MeOH)]. A minor
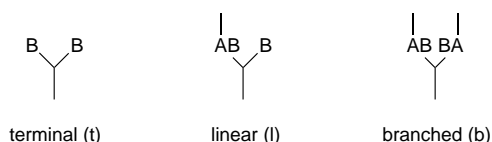

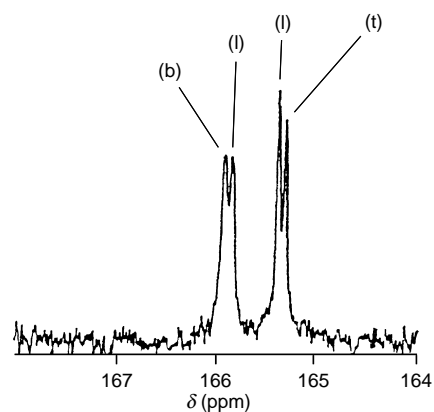**Fig. 1** Structural sub-units of an AB_2 hyperbranched polymer

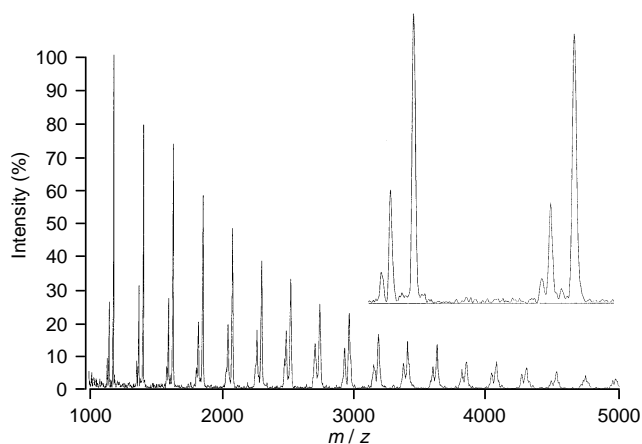**Fig. 2** ^{13}C NMR peak assignments for ester carbonyls

Fig. 3 MALDI-TOF spectrum. Inset: region *m/z* 1340–1680

Fig. 4 MALDI-TOF spectra for varying reaction times: (*a*) 1, (*b*) 2 and (*c*) 24 h

series of peaks is observed 32 mass units behind the main series. This is 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, particularly for high mass species, 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 relative proportion of the cyclic oligomers increases with increasing oligomer size. For higher molecular weight polymers produced at longer reaction times *only* cyclic oligomers are observed. In the case of the AB_2/B_x copolymers ($n = 2$, $x = 2$ or 3) two series of ions are observed attributable to polymer incorporating a core molecule and cyclic oligomers but no simple non-cyclic AB_2 oligomers. Cyclic structures predominate at low core to monomer ratios, whereas core terminated oligomers are more abundant at high core ratios.

This work clearly established that in AB_2 step growth polymerisations the outcome cannot be predicted by simple generalisations but is a sensitive function of monomer structure, reactions conditions and duration. In particular cyclisation, which can be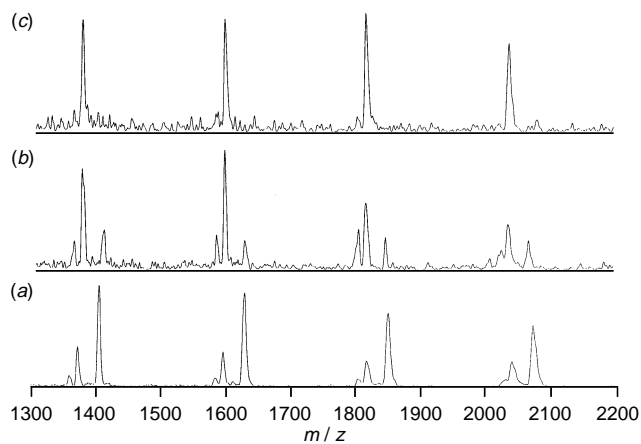 growth terminating, occurs readily in the systems described here and becomes easier as the monomers become larger and more flexible. This observation is not unexpected but appears to have been overlooked previously.

Footnote and References

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