A novel hyperbranched polyether by melt transetherification

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Melt self-condensation of 1-(2-hydroxyethoxy)-3,5-bis-(methoxymethyl)-2,4,6-trimethylbenzene in the presence of an acid catalyst *via* a transetherification process yielded a soluble high molecular weight hyperbranched polyether, whose structure was established by NMR spectroscopy.

Highly branched macromolecules, such as dendrimers and hyperbranched polymers, adopt compact conformations and possess a large number of terminal functional groups. This drastically alters both their solution and bulk properties. Several reviews have appeared in the recent literature, that describe the synthesis, structural properties and applications of dendrimers and hyperbranched polymers.[1–4] Despite the presence of significant levels of structural imperfections, hyperbranched polymers present one major advantage over their structurally perfect cousins and that is the ease of synthesis, which is most often a one-pot self-condensation of an AB$_2$-type monomer. More importantly, several of the interesting *dendrimeric* properties, such as low melt-viscosity and high functionality, are also exhibited by hyperbranched polymers, thereby making them excellent alternatives to the synthetically cumbersome dendrimers for certain kinds of applications. A large variety of hyperbranched polymers, namely polyesters, polyurethanes, polyamides, polyphenylenes, polysiloxanes, polycarbonates and polyethers have been reported.[3,4] One important feature of the polyether class is their high solubility in common organic solvents, which make them more readily amenable for the study and exploitation of their properties in solution. Hyperbranched polyethers of several types have also been reported in the literature.[5–8] Most of these procedures yielded moderate to high molecular weight polymers, however, they lack adaptability toward structural variation, in that they always require a phenolic group and an aryl/benzyl halide.

Recently, we reported a melt transetherification methodology for the synthesis of linear polyethers.[9] Fully substituted bisbenzyl methyl ethers readily underwent *melt-condensation* with diols in the presence of an acid catalyst to give polyethers of moderate molecular weights. In this report the transetherification methodology is extended for the preparation of a hyperbranched polyether under *melt* condition. For this purpose an AB$_2$ monomer having a hydroxy group (A) and two benzyl methyl ether groups (B) was targeted. An additional requirement for the transetherification approach to function effectively without crosslinking is the preclusion electrophilic aromatic substitution, which is fulfilled by complete substitution of all the aromatic sites in the monomer.[9] The simplest monomer that meets all these criteria is 1-(2-hydroxyethoxy)-3,5-bis(methoxymethyl)-2,4,6-trimethylbenzene (**3**), which is readily prepared from commercially available mesitol, as shown in Scheme 1. Mesitol was bis-chloromethylated and reacted with NaOCH$_3$–methanol to give the intermediate **2** in good yield. It

was then treated with 2-chloroethanol to give the monomer **3**. This monomer was readily polymerized at 145–150 °C in the presence of toulene-*p*-sulfonic acid (PTSA) as catalyst. Typically, the polymerization is carried out under N$_2$ purge for 30 min and then under reduced pressure (0.01 mm of Hg) for an additional 15 min to attain high molecular weight. To start with, the contents of the reaction vessel formed a clear melt but as the condensation proceeded it transformed into a solid mass. The solid polymer was dissolved in THF, filtered to remove any unwanted insoluble material, and then precipitated into methanol. The precipitate was isolated and dried to give the polymer in 82% yield. The expected structure of the resulting hyperbranched polyether is shown in Scheme 1.

The ^{1}H-NMR spectra of the monomer **3** and the polymer are shown in Fig. 1, along with the assignments of the various peaks. Comparison of the spectrum of the monomer with that of the polymer reveals several interesting features. Firstly, as expected for high conversions, there is a 50% decrease in the relative intensity of the peak **d**, corresponding to Ar-CH$_2$OCH$_3$ protons, and a complete disappearance of the peak **b**, corresponding to the –CH$_2$OH protons, in the spectrum of the polymer (Fig. 1-B). Furthermore, two types of benzylic protons (**a$_1$** and **a$_2$**) of equal intensity—one corresponding to benzyl methyl ether (Ar-CH$_2$OCH$_3$) and the other to the reacted one (Ar-CH$_2$OR–), are seen in the polymer spectrum. These observations confirm that the transetherification process has indeed occurred to very high conversions to yield a polymer with the expected structure. One other interesting feature is the transformation of the peaks corresponding to the aromatic methyl groups from two singlets (**e** and **f**) in the monomer to a cluster of at least five well-resolved peaks (six inclusive of a shoulder), suggesting the presence of several distinct chemical environments in which they are present.

In general, hyperbranched polymers are expected to have different types of subunits, such as dendritic (D), linear (L) and terminal (T) units. Most often, the presence of these various units is established and quantified based on the ^{1}H-NMR signals corresponding to the aromatic protons belonging to them. Interestingly, in the present polyether a significantly more intense Ar-CH$_3$ signal appears to reveal the presence of these subunits. A total of six aromatic methyl signals (in the region between 2.3–2.5 ppm) are seen, as opposed to a total of seven that might be expected if no coincidental overlaps are present—two each corresponding to dendritic and terminal units and three to the linear unit. As expected, the sum total of the intensities of these Ar-CH$_3$ peaks is in the expected ratio with respect to the other peaks, **c** and **d**. In order to calculate the degree of branching (DB), it is essential to identify and quantify the mole fraction of the various subunits D, L and T, in such hyperbranched structures. Based on topological considerations
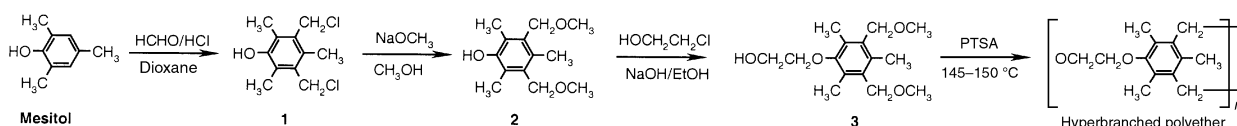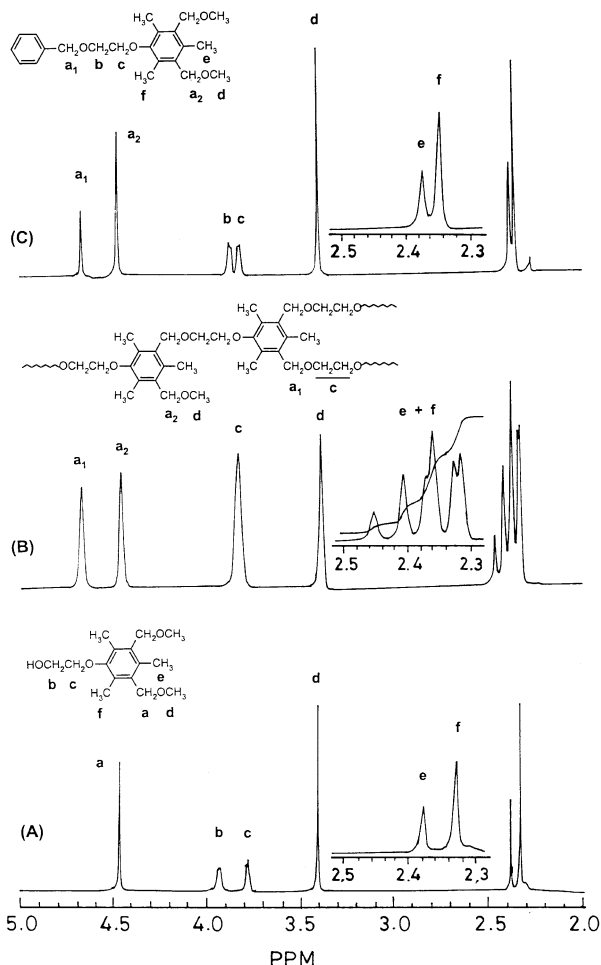

Scheme 1

Fig. 1 500 MHz ^{1}H-NMR spectra of the monomer (A), polymer (b) and model compound (C), in CDCl$_3$.

it has been shown that hyperbranched structures will always possess equal number of D and T units (at high conversions), and the DB has been calculated for several polymers using a simplified expression (eqn. 1), from the mole fraction of the terminal units alone.[8,10–13]

$$\text{DB} = \frac{[D]+[T]}{[D]+[L]+[T]} = \frac{2[T]}{[D]+[L]+[T]} \quad (1)$$

In order to identify the methyl peaks belonging to the terminal units, a model compound **4** (see Fig. 1-C) was prepared by reacting **2** with 2-benzyloxy-1-chloroethane in presence of a base, and its ^{1}H-NMR spectrum is shown in Fig. 1. Upon comparison of the spectrum of the model compound with that of the polymer, it is clear that the peaks between 2.34–2.39 ppm in the polymer corresponds to the Ar-C*H*$_3$ protons of the terminal unit. The sensitivity of the chemical shifts of these methyl protons to its chemical environment is apparent when one compares the spectrum of model compound **4** with that of the monomer; the transformation of a remote hydroxy group to a benzyl ether causes a significant downfield shift of the two *ortho*-methyl protons peak, **f**. Thus, a non-exact match between the chemical shifts of model compound **4** and the polymer is not surprising; the *ortho*-methyl signal **f** appears slightly further downfield in the polymer. Thus, the DB was calculated from the relative intensities of the two peaks assigned to the terminal unit (between 2.34–2.39 ppm) with respect to the total intensity of all the methyl signals (between 2.3–2.49 ppm), as per the above formula. This number works out to be 0.78 suggesting that a fairly high degree of branching has been achieved. In the absence of the dendritic model compound,[13] we rely on the *ca.* 1:2 intensity ratio of the shoulder to peak (**e**:**f**) in the polymer spectrum to confirm the absence of peaks due to other subunits within this one. Typical values for DB quoted in the literature range from 0.4–0.8.[14] Special efforts using a gradual addition of the AB$_2$ monomer to a polyfunctional B-type core monomer (B$_f$), are often needed to further increase the degree of branching.[15]

The molecular weight of the polymer was determined by GPC using polystyrene standards and it showed a broad distribution with M_W of 103 000 and a polydispersity of 5.8. The high polydispersity is typical of such hyperbranched structures. The DSC thermogram of the polymer was recorded under a dry N$_2$ purge, and the sample was first heated to 150 °C and then quenched to −100 °C at 30 °C min^{-1}. It was then reheated from −100 to 150 °C at 10 °C min^{-1} and cooled at the same rate to record the thermograms. No crystallization and melting transitions were observed either during the heating or cooling runs, which suggests that the samples were completely amorphous. A glass transition temperature (T_g) was, however, clearly visible at 28 °C.

In conclusion, we have shown that the *melt transetherification* approach can be readily adapted for the preparation of hyperbranched polyethers. More importantly, the intermediate **2** is readily amenable to a variety of structural variation by incorporation of various types of alkyl and oligoethyleneoxy spacers, to generate a wide range of AB$_2$ monomers. Such an inclusion of spacer segments into hyperbranched polyethers is not readily possible using most other previous methods, which makes this approach especially useful for preparing a range of hyperbranched structures starting from a single intermediate. A particularly interesting series of hyperbranched polyethers would be the one that incorporates oligoethyleneoxy segments. This would lead essentially to branched polyethylene oxides, which could serve as potential candidates for solid polymer electrolyte applications.[16,17] Work along these lines is currently in progress and will be reported shortly.

Notes and references

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