Polymer Bulletin 29, 265–270 (1992)

Polymer Bulletin

The synthesis and properties of a series of aromatic dendritic polyamides

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Summary

A series of three aromatic polyamide dendrimers are reported. The materials were prepared via a convergent growth approach and are monodisperse by GPC. We have analysed the dendrimers by a variety of standard techniques and report some conformational effects that can be observed in their ^{1}H NMR spectra.

Introduction

Dendritic polymers are attracting wide interest(1). The novel three dimensional and highly specific molecular architecture characteristic of dendrimers gives rise to a class of polymers which are different both to conventional linear or lightly branched polymers, and to networks. The synthesis of dendrimers via divergent and convergent approaches is now well documented and a variety of structures with a range of linking groups have been described(2). In this paper we report the synthesis of a series of three all aromatic polyamide dendrimers prepared via a convergent growth approach. The materials are highly branched analogues of commercially important polyamides such as Kevlar and Nomex, polymers which are characterised by their high thermal stability and low solubility(3). Dendritic polymers have been reported to show unusual solubility properties, for example, polyphenylenes are well known to be highly insoluble even at low molecular weights, whereas the dendritic polyphenylenes are soluble in common organic solvents such as chloroform and toluene(4). This illustrates one of the dramatic changes in property that can occur in going from a linear to a dendritic polymer, and given the commercial importance of linear polyamides, an investigation into the synthesis and properties of their dendritic analogues seems worthwhile.

Results and Discussion

Figure 1 shows the structure of the dendrimers which we have prepared. In order to simplify the difficult nomenclature of these materials we have used the terminology adopted by Miller and Neenan(5), whereby the dendrimers are named according to the number of benzene rings they contain. The wedges used to synthesise the dendrimers are named according to the number of benzene rings followed by the functionality at the focal point.

The simplest dendrimer [4] (not strictly a dendrimer according to Tomalia's definition since it has no branch points) was prepared by the reaction of 1,3,5-benzenetricarbonyl trichloride and aniline. This compound has been reported previously and our spectroscopic

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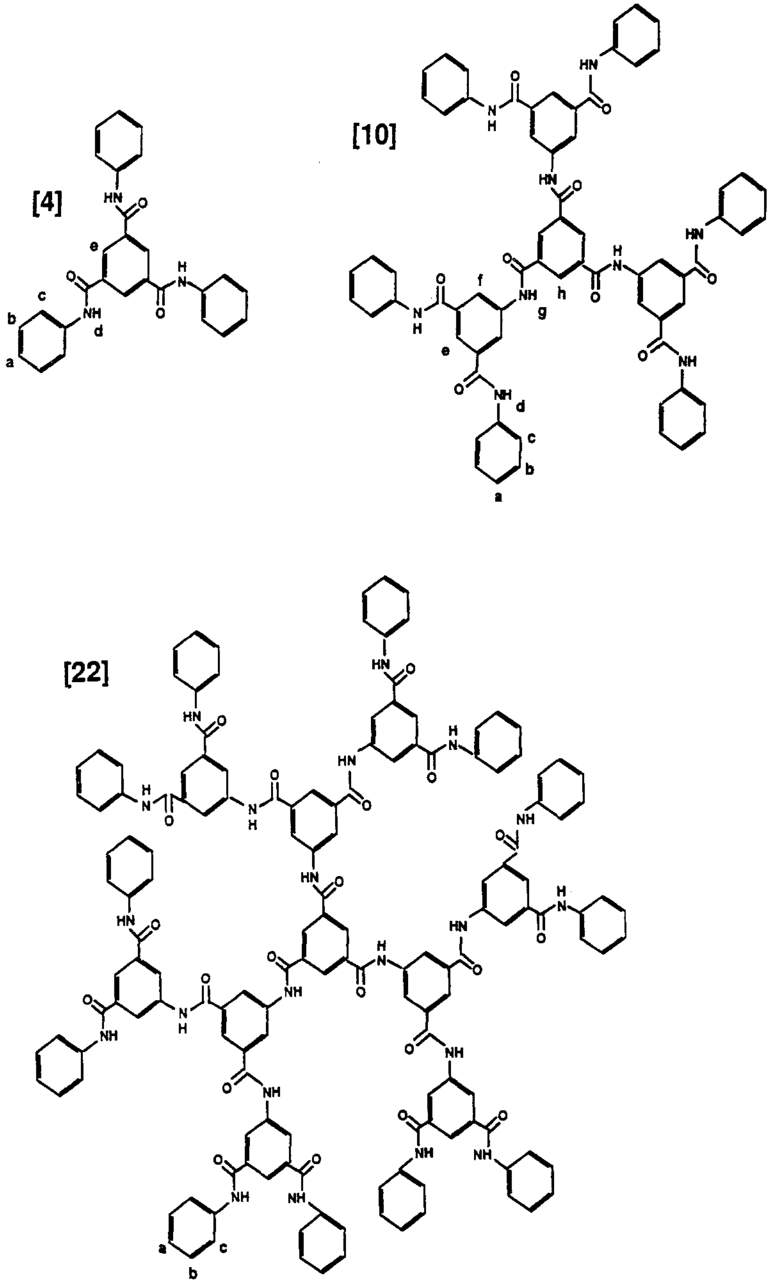

Figure 1 Structure of dendrimers [4], [10], and [22].

data are in good agreement with the limited, unreproduced and unassigned data given previously(4). However, we observe fewer ^{13}C NMR resonances suggesting that the previously reported samples were marginally contaminated.

The second generation dendrimer [10] has also been reported previously, but we disclose a slightly modified synthetic route and also some additional spectroscopic data where we observe some unusual results. Dendrimer [10] was prepared via the reaction between the core molecule 1,3,5-benzenetricarbonyl trichloride and [3]NH_2 in pyridine. The synthesis of the amine functionalised wedge is outlined in Figure 2.

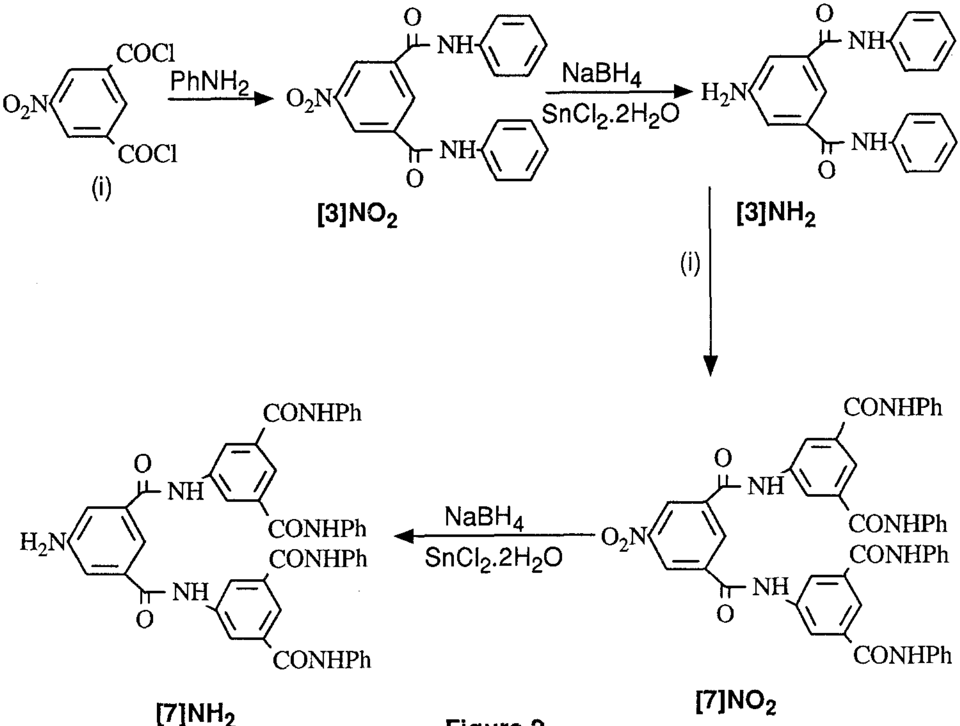

Figure 2

The reaction between 5-nitroisophthaloyl dichloride and two equivalents of aniline gave the nitro functionalised wedge [3]NO_2, which was then reduced using a combination of tin(II) chloride and sodium borohydride in ethanol. The combination of the two reducing agents appears to be critical; attempts to reduce the nitro group using only one of the reagents were not successful. Addition of the wedge to the core molecule using pyridine as base gave the dendrimer [10] which was purified by repeated reprecipitation from acetone solution into petroleum ether, to give an off white powder.

Dendrimer [22] was prepared by reaction of [7]NH_2 and the core molecule. The wedge was prepared as shown in Figure 2, via the reaction of two equivalents of [3]NH_2 and 5-nitroisophthaloyl dichloride in pyridine. Reduction of the nitro group using sodium borohydride and tin(II) chloride gave the amine functionalised wedge. Again the dendrimer was obtained as an off white powder after reprecipitation.

All compounds were characterised by a range of standard techniques. Figure 3 shows the ^1H 399.952MHz NMR spectra of the three dendrimers. In all cases the hydrogens of the outer phenyl ring are observed as multiplets in the 7.00ppm to 7.80ppm region. As

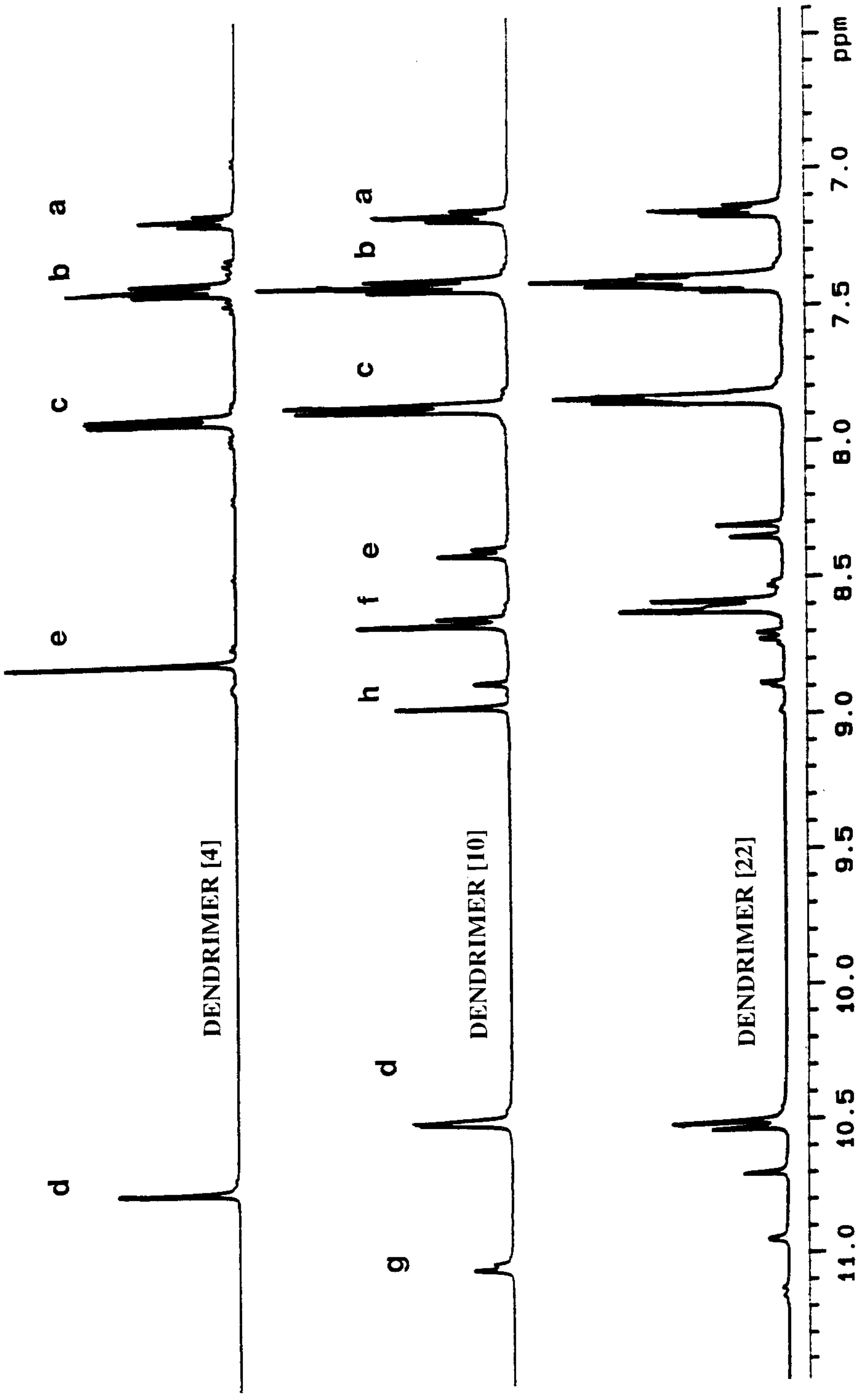

Figure 3 ^{1}H NMR Spectra of dendrimers [4], [10], and [22] recorded at 399.952MHz expected, for dendrimer[4], two additional singlets are observed for the core hydrogens and the amide N-H hydrogens.

Dendrimer [10] gives two signals in a 2:1 ratio at 10.52ppm and 11.21ppm, assigned to the amide hydrogens. The resonance at 11.21ppm is partially resolved as two signals also in a 2:1 ratio, suggesting two environments for the amide hydrogens nearest the core. Three further pairs of signals are observed, at 8.94 and 8.85ppm, 8.63 and 8.61ppm, and 8.38 and 8.36ppm. Integration shows the signals within each pair appear in a 2:1 ratio. The overall ratio of the pairs of signals is 1:2:1. This allows the pair of signals at 8.63 and 8.61ppm to be assigned to the hydrogens labelled (f). By comparison with model compounds the signals at 8.94 and 8.85ppm are assigned to the core hydrogens(h) and at 8.38 and 8.36ppm to hydrogens (e). It is evident that in the interior of the dendrimer the hydrogen signals which we initially expected to observe as singlets, show resolution indicative of more than one environment. We think that the most likely explanation of this will rest on the effect of different possible conformations within the dendrimer. The amide bonds have a trans geometry since cis conformations are extremely unlikely on stability grounds and in view of steric restrictions. Observation of molecular models shows that to accommodate the steric bulk of the substituents the plane of the amide bond will be twisted out of the plane of the aromatic rings. A completely planar structure would quickly become impossibly congested. Therefore, the possibility of ordering the carbonyl groups around the core must be considered. The conformation with all the carbonyl groups pointing in one direction appears extremely unlikely on steric grounds. The conformation with two carbonyl groups pointing in similar directions with one opposed seems much more favourable sterically, and is consistent with the repeated resolution of signals in a 2:1 intensity ratio which we observe in the NMR spectrum. It is therefore possible that we have prepared dendrimer [10] as one conformation with restricted rotation allowing resolution of seemingly equivalent protons in the NMR spectrum. Free rotation of the external unhindered aromatic rings results in observation of the expected spectrum of a mobile phenyl unit. Similar resolution of signals was observed in the ^{13}C NMR spectrum; carbon resonances associated with the interior of the dendrimer are seen as two resolved signals and carbon signals associated with the exterior are seen as unresolved signals.

The ^{1}H NMR spectrum of the third generation dendrimer [22] is also shown in Figure 3. The spectrum is complex; in this case the amide hydrogens are resolved into six signals, resulting from two possible environments for the inner amide hydrogens, three environments for the next layer of amide protons, and one environment for the outer amide hydrogens. A completely satisfactory rationalisation of these observations in terms of conformational preferences has not been accomplished.

All the materials display a single peak by GPC, (THF, Viscotek instrument equipped with two mixed columns of PL-gel, Polymer Laboratories Ltd.) the observed molecular weight increasing gradually with generation and all compounds being monodisperse.

The materials have been investigated using wide angle X-ray scattering which indicates that [4] is highly crystalline, and [10] and [22] are not significantly ordered at the scale of the analysis. The high crystallinity of [4] is not surprising, the relatively small size of the molecule allowing it to pack efficiently.This trend is reflected in solubility data, where solubilities of 24g/l, 298g/l, and 40g/l in THF at room temperature were obtained for dendrimers [4], [10], and [22] respectively. This dramatic increase in solubility from the first to second generation, followed by a rapid decrease from the second to the third generation is somewhat surprising.

Conclusions

We have prepared and characterised a series of all aromatic polyamide dendrimers. We have observed a number of trends in the behaviour of the materials and report some resolution of signals in the NMR spectra which have not been described previously. We are continuing with the analysis of the compounds and are extending the approach to the synthesis of higher generation materials. In addition we are preparing analogues with controlled surface functionality.

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Accepted August 11, 1992 C