# Dendritic solution viscosity behaviour in core terminated hyperbranched poly(amidoamine)s

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**A poly(amidoamine) hyperbranched $AB_2/B_6$ copolymer displays a viscosity/molecular weight profile similar to that shown by perfectly regular dendrimers.**

The physical properties of a polymer are heavily dependent upon its topology.[1–6] Dendrimers, prepared by stepwise iterative syntheses, represent a particularly interesting class of materials which are attracting considerable attention at present. A characterising feature of dendritic polymers is that past a critical point, their intrinsic viscosity decreases with increasing molecular weight.[7] It is often argued that the properties which distinguish dendrimers from other structures are associated only with those materials whose molecular weight is above this peak in the viscosity *versus* molecular weight curve.[8]

We have recently established a simple ‘one-pot’ route to the hyperbranched analogues of Tomalia’s poly(amidoamine) dendrimers.[9,10] These polymers, prepared by the melt polymerisation of *N*-acryloyl-α,β-diaminoalkane hydrochlorides[11] $H_2C{=}CHCONH(CH_2)_nNH_3^+Cl^-$ ($n$ = 2–7), exhibit a degree of branching approaching one in the case where $n$ = 2. The observation of near perfect branching for this monomer is very unusual indeed; so far it is the only example we have found in more than twelve $AB_2$ polymer systems studied. Near perfect branching in $AB_n$ systems does not, of course, imply the formation of materials with dendritic topology. This is illustrated in Fig. 1, where structure (*b*) represents one possible topology in the spectrum between the linear structure (*a*) and the perfect dendritic wedge (*c*), all of which display a branching factor of one.

The peak in the log (molecular weight) *versus* log (intrinsic viscosity) relationship is widely believed to be a specific characteristic of dendritic materials and the possibility of regulating the molecular weight *versus* viscosity relationship within the limits defined by linear and true dendritic systems has technological attractions.

Here we report the preparation of a series of $AB_2/B_6$ copolymers, using the monomer *N*-acryloyl-1,2-diaminoethane hydrochloride ($n$ = 2) in conjunction with the $B_6$ core, tris(2-aminoethyl)amine. The polymerisations were carried out under dry nitrogen in the melt and it was readily shown by $^1H$ NMR spectroscopy that the vinyl unit was rapidly and completely consumed in this system. For related monomers where $n > 2$ this did not occur and vinyl units remained after several hours reaction time. The high reactivity and high branching factor appears to be unique to the monomer where $n$ = 2. Since consumption of the monomer was complete, variation of the molar ratio of core terminating tris(2-aminoethyl)amine to $AB_2$ *N*-acryloyl-1,2-diaminoethane hydrochloride monomer allows regulation of product molecular weight. Unfortunately the water soluble polyelectrolytes produced in this work are not amenable to reliable molecular weight analysis by either GPC or MALDI–TOF MS, which prevents a direct check on their molecular weights and molecular weight distributions. However the knowledge that all the $AB_2$ wedges are terminated by cores and that all the monomers are consumed, taken with our earlier experience with less highly branched core-terminated polyesters,[12] gives some confidence in the calculated molecular weights used below. Our earlier work with $CHCl_3$ and THF soluble polyesters had established that the homo-$AB_2$ hyperbranched polyesters conformed to the Mark–Houwink relationship and that molecular weights calculated from $AB_2$ monomer to $B_n$ core molar ratios for the core terminated samples fell between the *M*n and *M*w values determined by GPC (see Fig. 2 in ref. 12), thus establishing a correlation between the molecular weight of the products and the $B_n$ core: $AB_2$ monomer molar ratio used in the polymerisation. Following this precedent, we have polymerised $AB_2/B_6$ mixtures with the molar ratios appropriate to the formation of successive generations of ideal dendrimers. Solution viscosity measurements on the resultant polyelectrolytes were carried out in 1% aqueous LiCl at 25 °C over a range of dilutions, using a Laude/Schott automated system. A plot of reduced viscosity against concentration allows extrapolation to zero concentration to give a value for intrinsic viscosity ($cm^3\ g^{-1}$).

The logs of the observed intrinsic viscosities were plotted against the logs of molecular weights calculated from the monomer to core terminator molar ratios and are shown in Fig. 2 in comparison with Tomalia’s PAMAM dendrimer data.[13] We

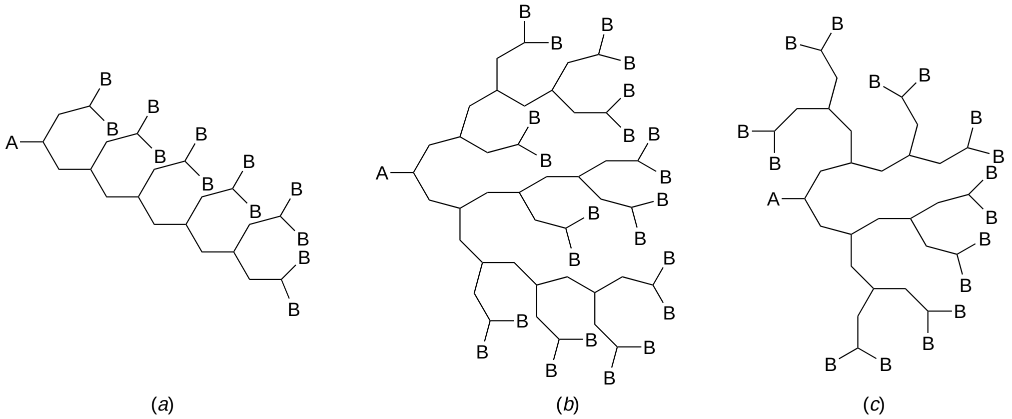

**Fig. 1** Possible structures of an $AB_2$ hyperbranched polymer with a branching factor of one

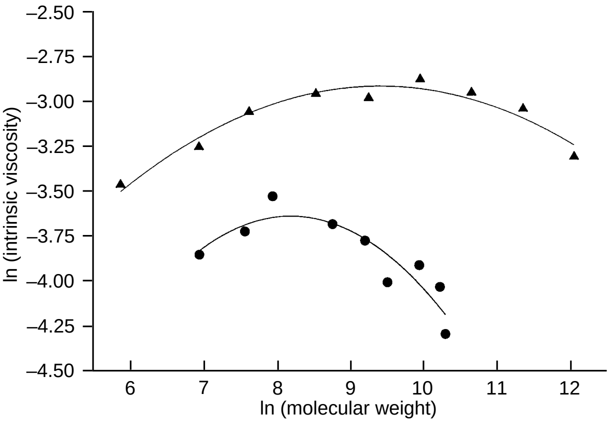

**Fig. 2** The molecular weight *vs.* intrinsic viscosity relationship for AB$_2$/B$_6$ copolymers: (●) AB$_2$/B$_6$ copolymers and (▲) Tomalia's PAMAM dendrimers (ref. 13)

do not expect that this simple 'one pot' synthesis will produce perfect monodisperse dendrimers; indeed, a distribution in both molecular weight and structure is to be expected. However it is clear that in the system examined the peak in the graph of log (intrinsic viscosity) *versus* calculated molecular weight is demonstrated and is consistent with the formation of polymeric materials with topologies giving rise to solution viscosity behaviour resembling that of dendrimers. These observations imply that at least some of the attractive materials properties of dendrimers may be obtained in materials synthesised by less laborious procedures than those reported to date.

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## Footnote and References

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