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HyperMacs. Long Chain Branched Analogues of Hyperbranched Polymers Prepared by the Polycondensation of AB_2 Macromonomers

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Summary: We describe here a new strategy for the synthesis of polymers with highly branched architectures. The strategy involves the synthesis by anionic polymerization of well-defined AB_2 polystyrene macromonomers with molecular weights from 3,600 to 94,000 $gmol^{-1}$, which are then converted via a one-pot polycondensation reaction into high molecular weight, long-chain (hyper)branched architectures. Since the *Hyper*branched structures are built up from condensation *Mac*romonomers we have coined the term 'HyperMac' to describe these branched polymers. In this paper we report the synthesis of the HyperMacs, the optimal conditions for the polycondensation reaction and some preliminary characterization studies.

Keywords: anionic polymerization; hyperbranched; macromonomers

Introduction

The physical properties of branched polymers differ significantly from linear polymers of equivalent molecular weight. The design and synthesis of new, well-defined molecular architectures such as star branched polymers[1,2], mikto star polymers[3–5] and H-shaped polymers[6,7] has contributed much to understanding and prediction of the relationship between structure and properties. The major synthetic method used to provide these polymers has been a combination of anionic polymerisation and carbosilane coupling reactions but the range of molecular architectures accessible by this method alone is restricted. More recently syntheses of dendrigraft, dendritically branched and arborescent[8–13] polymers with a higher degree and complexity of branching have been published, much of this work has recently been reviewed by Gautier and Teertstra[14]. A number of examples of well defined dendritically branched polymers, essentially analogues of classical dendrimers with an additional polymer chain between branch points have been reported, notably by Gnanou[8], Hedrick[15] and more recently Hirao[16]. In these cases the structures are well-defined in terms of molecular weight and polydispersity but the methodology involves many iterative steps usually involving a series of living or controlled polymerization, functionalization and deprotection steps. A more facile approach has been reported by Knauss et al[9–11] who utilises a coupling agent in convergent living anionic polymerization to produce polymers with dendritic branching in a one pot reaction, although, this approach results in a distribution of molecular weights between branch points and a distribution of branching structures, more like that of hyperbranched polymers. The motivation for much of the above work is to provide 'model' long chain branched materials to help elucidate the relationship between molecular architecture and the physical properties of polymers, specifically the effect of long-chain branching on rheology. In this paper we describe a strategy to

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synthesize long-chain (hyper)branched polymers (HyperMacs) by the polycondensation of an AB_2 macromonomer. The macromonomers are synthesized by anionic polymerization and as such are well defined in terms of both molecular weight and polydispersity and the HyperMacs are produced in a facile one-pot polycondensation. The use of anionic polymerization for the synthesis of the condensation macromonomers in the present work allows the synthesis of macromonomers with molecular weights from a few hundred to tens of thousands $gmol^{-1}$. This control offers the possibility of varying the molecular weight between branch points from below the entanglement molecular weight, M_e, to many times M_e. However the inherantly imperfect nature of the branched structure produced by the AB_2 polycondensation reaction does not allow the for the production of a uniform molecular weight between branch points. In theory (but not yet in reality) the synthesis and condensation of block copolymeric macromonomers is also feasible making this a very versatile methodology. We have used a Williamson coupling reaction to yield an ether linkage in a similar fashion to that used by Fréchet in the synthesis of classical hyperbranched and dendritic polyethers[17,18]. This type of reaction has been shown to be viable by Fréchet who used this coupling reaction to successfully prepare a sixth generation dendrimer with a nominal molecular weight of 13,542 Daltons and hyperbranched polyethers with molecular weights (by light scattering) in excess of 100,000 Daltons. Furthermore the linkage is stable and the functionalities required on the macromonomer can be readily introduced with the aid of some simple protection/deprotection and end group modification chemistry. In outline the approach described involves the synthesis of well-defined AB_2 macromonomers by anionic polymerization using a lithium initiator containing a protected primary alcohol functionality. The living polymer is then end capped with a diphenylethylene derivative containing two protected phenol groups. Following deprotection of the functional groups and conversion of the primary alcohol group into an alkyl chloride, the macromonomer can be converted into a HyperMac polymer via a step growth Williamson coupling reaction.

Experimental

Materials

Benzene (HPLC grade, Aldrich) and styrene (Aldrich) were both dried and degassed over CaH2 (Aldrich), styrene was further purified with dibutylmagnesium immediately prior to use. N,N,N′,N′-Tetramethylethylenediamine (Aldrich) and 3-tert-butyldimethylsiloxy-1-propyllithium, 0.7 M in cyclohexane (InitiaLi 103, FMC corporation) were used as received. 1,1-Bis(4-tert-butyldimethylsiloxyphenyl)ethylene was synthesised in two steps from dihydroxybenzophenone according to the procedure of Quirk and Wang[19]. Thionyl chloride (99+%, Aldrich) and pyridine (anhydrous, Aldrich) were used as received. THF was purified by passing the solvent through a system of columns designed to remove both protic impurities and oxygen[20]. 18-Crown-6-ether and potassium carbonate powder, 325 mesh (both Aldrich) were dried in a vacuum oven and stored in a vacuum desiccator.

Measurements

Molecular weight analysis of both the macromonomers and HyperMacs was carried out by triple detection (with angular correction) size exclusion chromatography (SEC) on a Viscotek TDA 302 with refractive index, viscosity and right angle light scattering detectors. A value of 0.185 (obtained from Viscotek) was used for the dn/dc of polystyrene. 2 × 300 mm PLgel 5 μm mixed C columns (with a linear range of molecular weight from 200–2,000,000 $gmol^{-1}$) were employed, THF was used as the eluent with a flow rate of 1.0 ml/min at a temperature of 30 °C. The coupling reactions were monitored and further analysed by SEC using a Viscotek 200 with a refractive index detector and 3 × 300 mm PLgel 5 μm 10^4 Å high-resolution columns (with an effective molecular weight range of 10,000–600,000 gmol^{-1}), THF was used as the eluent at a flow rate of 1.0 ml/min. ^{1}H-NMR analysis was carried out on either a Varian Inova-500 MHz or Mercury-400 MHz spectrometer using C_6D_6 as a solvent. Spectra were referenced to the trace of C_6H_6 (7.2 ppm) present in the C_6D_6.

Synthesis of AB_2 Macromonomer-$(OH)_3$ Protected (III)

All polymerizations were carried out using standard high vacuum techniques, at room temperature with benzene as the solvent. A typical macromonomer polymerization was as follows. 500 ml of benzene and 50 g (0.48 mol) of styrene were distilled, under vacuum, into a 1-litre reaction flask. To the monomer solution was added tetramethylethylenediamine (TMEDA) 1 mole equivalent with respect to lithium initiator and then 3-*tert*-butyldimethylsiloxy-1-propyllithium, 0.7 M in cyclohexane **(I)** as the initiator, the latter being injected through a septum. For a target M_n of 10,000 gmol^{-1} we used 0.755 ml (5 mmol) TMEDA and 7.14 ml initiator (5 mmol). Upon addition of the initiator to the reaction mixture, the orange/red colour of living polystyryllithium was observed. The solution was stirred for one hour to allow complete propagation before a small sample of polymer solution (for molecular weight/nmr analysis) was removed and terminated with nitrogen sparged methanol. To the remaining living polymer solution was added 1,1-*bis*(4-*tert*-butyldimethylsiloxyphenyl)ethylene **(II)** (1.5 molar equivalents w.r.t. lithium) as a solution in benzene. The reaction was stirred at room temperature for 5 days before the reaction was terminated with nitrogen sparged methanol. The polymer was recovered by precipitation in methanol, redissolved in benzene, reprecipitated once more into methanol and dried in vacuo. Yield >95%. M_n 12,400 gmol^{-1}, M_w 12,900 gmol^{-1} Pd 1.04. ^{1}H NMR (C_6D_6) $C\mathbf{H}_2OSi$ δ 3.36, $\mathbf{H}C(Ph)_2$ δ 3.5, $Si(CH_3)_2C(C\mathbf{H}_3)_3$ δ 1.0, $ArOSi(C\mathbf{H}_3)_2C(CH_3)$ δ 0.1, $CH_2OSi(C\mathbf{H}_3)_2C(CH_3)_3$ δ 0.0.

Synthesis of AB_2 Macromonomer-$(OH)_3$ Deprotected (IV)

The AB_2 macromonomer with all three alcohol groups protected by *tert*-butyldimethylsilyl (TBDMS) groups was dissolved in THF (10% w/v solution). To the solution was added drop wise, conc. HCl (37 wt %), mole ratio of acid:protected alcohol was 5:1. The solution was then warmed up to reflux and stirred at reflux overnight. The solution was cooled and the polymer recovered by precipitation into methanol, redissolved in benzene, reprecipitated once more into methanol and dried in vacuo at 50 °C for two days. Yield >95%. ^{1}H NMR (C_6D_6) $C\mathbf{H}_2OH$ δ 3.15, $\mathbf{H}O$-Ph δ 3.7–3.8.

Synthesis of AB_2 Macromonomer-$(OH)_2Cl$ (V Scheme 1). Chlorination of Primary Alcohol Group

In a 500 ml round bottom flask, 10 g of the deprotected AB_2 macromonomer (12,400 gmol^{-1}, 8.2×10^{-4} mol) was dissolved in 100 ml of benzene under an inert atmosphere of nitrogen gas. To this solution was added 0.52 g (6.6×10^{-3} mol) pyridine and the mixture stirred for 15 minutes before cooling to 0 °C with an ice/water bath. To the stirring solution was added 0.98 g (8.2×10^{-3} mol) of thionyl chloride over a period of 5 minutes before allowing the reaction mixture to rise to room temperature over an hour. The mixture was then warmed to 55 °C and stirred at this temperature overnight. A small aliquot was then removed for ^{1}H-NMR analysis (in C_6D_6) which confirmed that the signal for the CH_2-OH (3.15 ppm) had been completely replaced by a new signal for CH_2-Cl at 2.9 ppm. The remaining polymer was recovered in quantitative yield by precipitation into methanol. The product was collected by filtration, redissolved in toluene and passed through a column of alumina to remove any residual traces of pyridine or thionyl chloride. The purified material was precipitated into methanol, collected by filtration and dried to constant mass in vacuo at 50 °C for several days.

AB$_2$ Macromonomer Polycondensation Coupling Reactions. HyperMac Synthesis

Coupling reactions were carried out under an inert atmosphere of either argon or nitrogen. Although the solution concentration was a parameter that was later varied, a typical polycondensation coupling reaction was carried out thus, 2 g of AB$_2$ macromonomer 3 (M$_n$ 12,400 gmol^{-1}, 1.6×10^{-4} mol), 0.09 g (6.5×10^{-4} mol) potassium carbonate and 0.17 g (6.5×10^{-4} mol) 18-crown-6-ether were dissolved in 10 ml of DMF. The solution temperature was raised to reflux using an oil bath and the mixture stirred vigorously. The progress of the coupling reaction was followed by extracting small samples periodically and subjecting the sample to size exclusion chromatography analysis. The reaction was deemed to be complete when no further increase in molecular weight was observed. In this case the reaction was complete after 2 hours. The mixture was then cooled and recovered by precipitation into methanol. The product was redissolved in benzene and reprecipitated once again into methanol before drying in vacuo. Yield 1.8 g (90%), M$_n$ 52,600 gmol^{-1}, M$_w$ 167,400 gmol^{-1}, PDI 3.2.

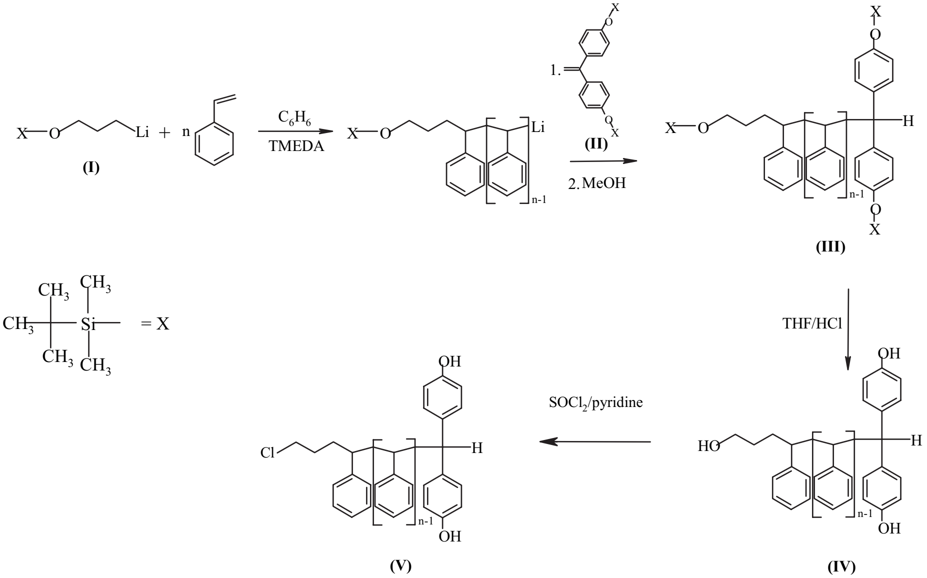
Results and Discussion

The living nature of anionic polymerization allows for the introduction of functional groups at either end of the polymer chain by using suitable initiators and terminating agents. AB$_2$ macromonomers have been prepared using a commercially available lithium initiator (containing a protected alcohol functionality). The living polymerization was end capped with a readily synthesized diphenylethylene derivative containing two protected phenol groups in a controlled termination reaction. Following deprotection of the alcohol groups and the chemical conversion of the primary alcohol group to an alkyl halide the AB$_2$ macromonomers have been used to build up novel, highly branched polymeric architectures

Synthesis of Macromonomers

When considering not only the design but also the synthesis of the macromonomer building blocks, our prime objectives were to quantitatively introduce the relevant functionalities that would facilitate subsequent Williamson coupling reactions but also to retain good control over both the molecular weight and the polydispersity of the macromonomers.

The polymers were initiated with 3-*tert*-butyldimethylsiloxy-1-propyllithium and were end capped with 1,1-*bis*(4-*tert*-butyldimethylsiloxyphenyl)ethylene, **II** (Reaction Scheme 1) to yield the fully protected AB$_2$ macromonomer **III**. Since this DPE derivative is known not to propagate[21] because of its steric bulkiness and reduced reactivity, it is possible to add an excess of this reagent w.r.t. lithium to facilitate this end capping reaction. Even so this is a slow reaction and the mixture was stirred for 5 days[19] at room temperature to ensure complete reaction. The macromonomers were then terminated with nitrogen-sparged methanol and recovered by precipitation in methanol, collected by filtration, redissolved in benzene and reprecipitated once again into methanol before drying to constant weight in vacuo. The TBDMS protection groups were removed by acid hydrolysis[19] by stirring the protected macromonomer **III** in THF solution under reflux in the presence of hydrochloric acid (added as a 10 M aqueous solution). The resulting deprotected macromonomer **IV** was recovered by precipitation into methanol, redissolved in benzene and reprecipitiated once more into methanol to ensure complete removal of all impurities. ^{1}H-NMR analysis showed no residual peaks corresponding to the TBDMS protection groups at 0.0, 0.1 and 1.0 ppm and a shift in the CH$_2$-OX end group from 3.36 ppm (CH$_2$OSi) to 3.15 ppm (CH$_2$OH) **(**see Figure 1 inset**)** confirming complete deprotection of all the alcohol



Scheme 1.
Synthesis of AB_2 polystyrene macromonomer.

groups. Furthermore, after deprotection a signal for the phenolic **OH** becomes apparent at 3.7–3.8 ppm (Figure 1), this signal disappears on shaking with D_20. Analysis of the integrations of the phenolic hydroxyl protons indicate greater than 90% functionalization, a number that is probably lower than the actual value due to exchange with traces of D_2O in the C_6D_6.

In order to couple the macromonomers via an ether linkage it is necessary to convert the primary alcohol group of (IV) into an alkyl halide group. The primary alcohol was converted quantitatively to an alkyl chloride group by reaction with thionyl chloride in benzene[22]. ^{1}H-NMR was used to follow this transformation, the broad signal at 3.15 ppm of the -$\mathbf{CH_2}$-OH completely disappears to be replaced with a new broad signal at 2.9 ppm corresponding to –$\mathbf{CH_2}$-Cl (see Figure 1 inset). Analysis of the integration ratio of –$\mathbf{CH_2}$-Cl versus the signal for the polystyrene aromatic protons (δ 6.2–7.2 ppm) confirms quantitative functionalization. A series of six AB_2 macromonomers have been prepared with molecular weights in the range 3,600 to 94,000 gmol^{-1} as shown in Table 1.

Synthesis of HyperMacs

Hyperbranched polymers, synthesised from AB_x monomers are prepared in a one-pot reaction with no protection/deprotection chemistry and as such are easily made on a large scale in a relatively short period of time, the resulting materials are highly but irregularly branched and polydisperse. The synthesis of HyperMacs from AB_2 macromonomers were similarly prepared in a one-pot reaction. The resulting polymers are also highly and irregularly branched materials with broad molecular weight distributions. They contain branched sections, linear sections and large numbers of end-groups. One further 'defect' that may arise as a result of these polycondensations is loop formation as a result of intramolecular cyclization. A Williamson coupling reaction to form an ether linkage has been used in the polycondensation and since C-alkylation is a well-known potential side reaction to the ether formation, the choice of solvent is very important in achieving efficiency of reaction and a low level of C-alkylation. Since the macromonomer coupling reaction will be promoted when carried out in a good solvent for the

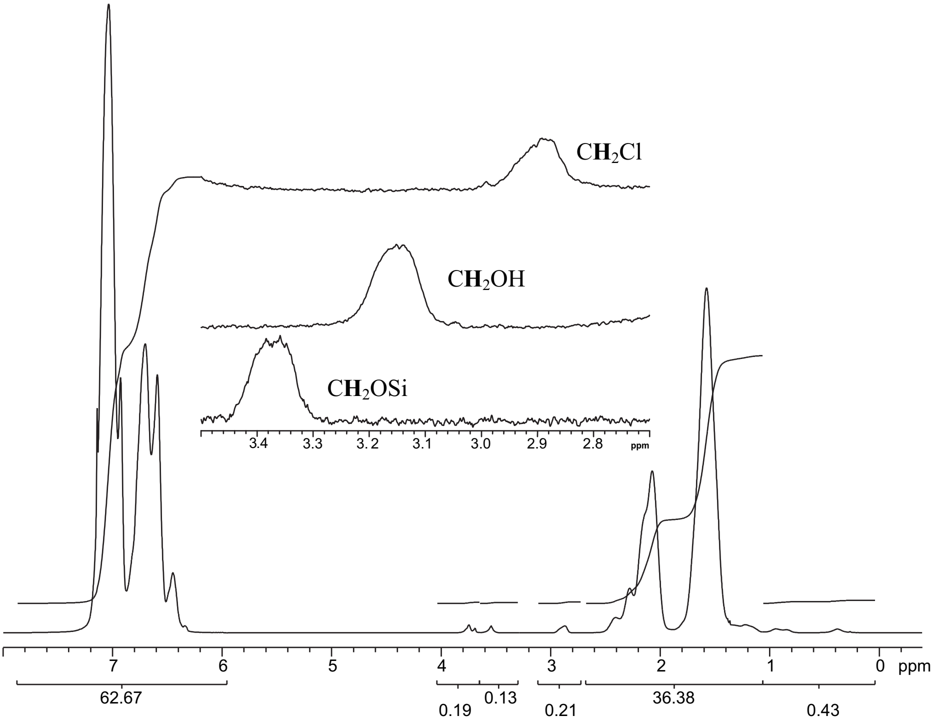


Figure 1.
^{1}H NMR (C_6D_6) of macromonomer 3 M_n 12,400 gmol^{-1}. Inset showing transformation of end group introduced at the initiating end of chain from protected alcohol (C**H**$_2$-O-Si) to primary alcohol (C**H**$_2$-OH) to alkyl chloride (C**H**$_2$-Cl), macromonomer 3.

polymer and Feuer and Hooz[23] suggest that ether formation is favoured (and C-alkylation minimised) by the use of aprotic solvents with a high dielectric constant we concluded that solvents such as THF and DMF would be suitable candidates and the use of both has been investigated. Furthermore we have investigated the influence of solution concentration on the polycondensation reaction and followed these reactions over time. In reactions such as this, intramolecular coupling reactions will always compete with intermolecular coupling reactions; an intramolecular reaction results in no increase in molecular weight and the formation of a loop and as such is undesirable. It is to be expected that intramolecular reactions will be favoured in more dilute solutions, and therefore we might expect lower molecular weight products under these conditions. The coupling reactions were typically carried out on a 2 g scale and their progress monitored by SEC using high-resolution columns, which result in far better separation of the eluting species enabling easier interpretation of the information. The results of the polycondensation of a 20 % w/v solution of macromonomers 1-6 (see

Table 1.
Molecular weight and polydispersity data for a series of polystyrene AB_2 macromonomers (V) synthesized by anionic polymerization according to Reaction Scheme 1.

Macromonomer	M_n/gmol^{-1}	M_w/gmol^{-1}	Pd
1	3,600	3,800	1.06
2	6,300	6,500	1.04
3	12,400	12,900	1.04
4	16,800	17,200	1.02
5	37,300	38,900	1.04
6	94,000	104,200	1.1

Table 2.
Molecular weight, polydispersity and intrinsic viscosity data for HyperMacs synthesized from macromonomers 1–6.

Macromonomer	M_n/gmol^{-1}	Dp_n	M_w/gmol^{-1}	Dp_w	PDI	$[\eta]_{hyp}$/dlg^{-1a}	$[\eta]_{lin}$/dlg^{-1b}	g′^{c}
1	16,100	4.5	36,600	9.6	2.2	0.15	0.23	0.65
2	33,600	5.3	65,400	10.1	1.9	0.23	0.34	0.67
3	52,600	4.2	167,000	13.0	3.2	0.42	0.67	0.63
4	88,000	5.2	298,000	17.3	3.4	0.57	1.01	0.56
5	185,000	5.0	556,000	14.3	3.0	0.94	1.58	0.59
6	565,400	6.0	1,630,000	15.6	2.9	1.81	3.39	0.53

[a] Measured by SEC viscometry.
[b] Calculated using the Mark-Houwink equation $[\eta] = KM^a$.
[c] $g' = [\eta]_{hyper}/[\eta]_{linear}$.

Table 1) in refluxing DMF are shown in Table 2.

In each case the polycondensation was successful and high molecular weight polymers with highly branched architectures were formed. There are a number of observations that we can make based on the data in Table 2. Firstly the degree of polycondensation is maybe not as high as might be expected for what is essentially a very rapid reaction. The reactions reach an end point in a matter of a few hours, depending on the molecular weight of macromonomer. As the molecular weight of the macromonomer decreases so do the times required to reach an end point in the polycondensation. Macromonomer 6 reached its end point after 5 hours, macromonomer 5 required 4 hours, macromonomers 3 and 4 requiring approximately 90 and 120 minutes respectively and macromonomers 1 and 2 both reaching an end point in less than an hour. These observations are not surprising and can be explained by decreasing concentration of reactive functionalities and increasing viscosities as the molecular weight of macromonomer increases. In all cases however the SEC chromatograms indicate the presence of polymer with the same molecular weight as the macromonomer starting material see Figure 2. In Figure 2 the peak at the highest retention volume has the same molecular weight as the starting material and suggests some limiting factor to the extent of reaction. In fact we believe there are two limiting factors which influence the extent of this reaction. A likely limiting factor is the presence of impurities in the DMF. Although the DMF is highly pure at the start of the reaction, it decomposes slowly at high temperatures to give small amounts of dimethylamine and carbon monoxide and this decomposition is catalysed by acidic or basic materials[24]. Nucleophilic attack by dimethylamine on the alkyl chloride functionality of the macromonomer or growing HyperMac is possible and although the concentration of impurities such as dimethylamine is likely to be low, the concentration of alkyl chloride functionality is also very low. The likelihood of deleterious side reactions is supported by ^{1}H-NMR analysis (Figure 3) of a HyperMac formed by such a polycondensation. Figure 3 shows the area of the spectrum in which you would expect to see any unreacted alkyl chloride (δ 2.9 ppm) and clearly there is no evidence of residual alkyl chloride groups. A second limiting factor is the competition between inter and intramolecular reaction as alluded to previously. This competition is impossible to avoid in the reaction of AB_2 (macro)monomers. Closer examination of the SEC chromatogram in Figure 2 confirms the presence of cyclisation. The bimodal peak at highest elution volume has the same molecular weight as the starting macromonomer but the "shoulder" at slightly higher retention volumes suggests that this bimodality arises from the presence of two species with slightly different hydrodymanic volumes. The

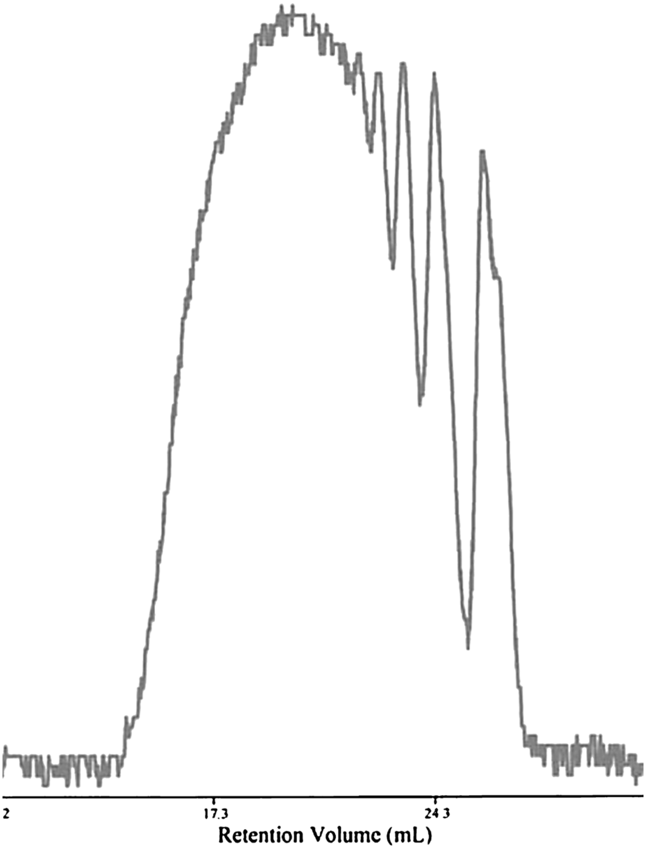


Figure 2.
Typical SEC chromatogram of a HyperMac.

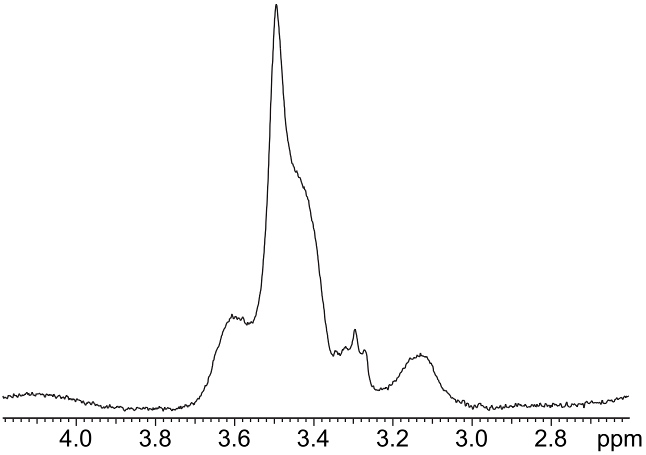


Figure 3.
^{1}H-NMR of HyperMac formed by the polycondensation of Macromonomer 3.

higher retention volume of the "shoulder" implies a smaller hydrodynamic volume which is consistant with the presence of cyclic polymer of the same molecular weight as the linear macromonomer. It is well known that cyclic polymer chains have a smaller hydrodynamic volume than their linear analogues[25]. We found not surprisingly that the rate of the coupling reaction in refluxing DMF was far higher than in refluxing THF, not only because of the difference in boiling point (153 °C for DMF and 67 °C for THF) but also because of the difference in dielectric constant (7.58 and 36.71 for THF and DMF at 25 °C respectively), the coupling reaction being favoured by solvents with high dielectric constants. In contrast to DMF, the reaction in THF did not proceed rapidly, after 150 minutes at reflux there was no apparent reaction and even after 5 days at reflux the extent of reaction was only a fraction of that observed in DMF.

However, without doubt the polycondensation reaction has occurred. To verify that the HyperMacs do in fact have a branched architecture and to get some idea of the degree of branching, the branching factor g' was calculated, g' being given by the ratio of the intrinsic viscosity of the branched polymer $[\eta]_{hyper}$ to the intrinsic viscosity of a linear polymer $[\eta]_{linear}$ of the same molecular weight[16,26]. Shown in Table 2 are g' values for each of the six HyperMacs. The intrinsic viscosity of the linear analogues were calculated using the Mark-Houwink equation with values of $a = 0.712$ and $K = 12.8 \times 10^{-5}$ dl/g (supplied by American Polymer Standards Corporation). In each case the branching factor g' is much less than 1.0 implying a more compact structure than the linear analogue, consistant with a highly branched architecture. It appears as if g' seems to be lower for HyperMacs made from the higher molecular weight macromonomers although the trend is debateable, in each case the value of g' falls within a fairly narrow range (0.53–0.67). The values compare very favourably with the data generated by Hirao et al.[16] for well-defined, narrow polydispersity dendrimer-like polymers. These authors found values of g' of 0.80, 0.59 and 0.46 for a first, second and third generation dendrimer-like polymethylmethacrylate. The second generation structure has a branched architecture containing 13 linear chains coupled together and the g' value of 0.59 is very similar to the data we have obtained for HyperMacs with Dp_w in the range 10–17. However, it should be noted that the values of g' should be considered with some caution since the intrinsic viscosity of the HyperMac is of a material which is not only polydisperse in molecular weight but also in molecular architecture whereas the intrinsic viscosity of the linear polymer is calculated from the Mark-Houwink equation and therefore the value represents that of a monodisperse polymer. More appropriate values of g' would be obtained by fractionating the HyperMac into a number of less polydisperse samples and repeating the measurements. This work is in progress and will be reported at a later date. Despite that caveat, the low values of g' undoubtedly confirms that these HyperMacs are highly branched.

It would also appear that there is a modest dependence on the extent of reaction with the molecular weight of macromonomer and it might be concluded that the higher molecular weight macromonomers underwent polycondensation to a higher degree than the lower molecular weight macromonomers. Although these six samples are too small a data set to make any firm conclusions, the degree of polycondensation, notably Dp_w, and polydispersity seem to increase with molecular weight of macromonomer.

The Influence of Solution Concentration

In light of the above findings on the occurrence of cyclization and reaction with impurities we hypothesized that both of these limitations could be controlled to a certain extent by varying the concentration of the macromonomer solution and we investigated the influence of the concentration of the macromonomer solution on the extent of polycondensation with the aim of minimizing intramolecular cyclization reactions and reactions with impurities. A series of 5 polycondensations was carried out using macromonomer 3 (M_n 12,400 $gmol^{-1}$) in which the concentration of the solution was varied from 5% to 40% w/v in DMF. Other than this, the ratio of macromonomer, crown ether and potassium carbonate remained constant. Each reaction was followed by SEC and was deemed to be complete when no further increase in molecular weight was observed. The concentration of reactants obviously had an impact on the rate of reaction; both of the reactions with a concentration of 30% and 40% showed no further increase in molecular weight after 1 hour, at 20% this time had increased to 90 minutes and for the most dilute solutions, 10% and 5% the times increased to 3 and 4 hours respectively. The HyperMacs produced in these experiments were analysed by SEC and the results are shown in Table 3 and Figure 4. It can be seen from both the chromatograms and the analysis that concentration has a dramatic effect on the extent of polycondensation. The data in Table 3 shows conclusively that as the concentration is increased there is a concomitant increase in the extent of polycondensation, as shown by increasing molecular weights and polydispersity. Although there appears to be no levelling off of this relationship, implying that further increases in concentration could result in greater increases in the extent of reaction it should be noted that the data for 40% w/v solution was for a sample extracted one hour after the reaction mixture had reached reflux. The reaction was then allowed to proceed overnight during which time the reaction had ceased stirring; SEC analysis of the final product showed some reduction in molecular weight with respect to the earlier sample, possibly due to thermal degradation. Whilst increasing the concentration beyond 40% w/v could lead to further increases in the extent of polycondensation, the reaction would need to be stirred more effectively and monitored closely.

The principle reason for the increased extent of polycondensation is as expected, i.e. at higher solution concentration intermolecular reaction is promoted at the expense of intramolecular reaction. This is evident in the SEC chromatograms of each reaction product (see Figure 4) in which we can see that the highest retention volume peak with a retention volume of approx 26–27 ml is bimodal, indicating the presence of both uncoupled starting macromonomer and the cyclized analogue, formed as a result of intramolecular coupling. At 5% solution concentration the cyclized macromonomer (to higher retention volumes) is the major component, at 10% the cyclized and linear macromonomer are present in almost equal quantities and at 20, 30 and 40% the cyclized macromonomer becomes the minor component, becoming least prevalent at 40%. Furthermore, the peak with a retention volume of approximately 24–25 ml also suggests a similar behaviour for the dimer. At 5% this peak is clearly unsymmetrical and skewed towards higher retention

Table 3.
SEC characterization data showing the affect of solution concentration on the synthesis of HyperMacs prepared using macromonomer 3.

Conc/% w/v	$M_n/gmol^{-1}$	Dp_n	$M_w/gmol^{-1}$	Dp_w	PDI	$[\eta]_{hyp}/dlg^{-1a}$	$[\eta]_{lin}/dlg^{-1b}$	g'^c
5	35,000	2.8	74,600	5.8	2.1	0.26	0.38	0.68
10	40,500	3.3	104,000	8.1	2.6	0.32	0.48	0.67
20	52,600	4.2	167,000	13.0	3.2	0.42	0.67	0.63
30	57,200	4.6	206,000	15.9	3.6	0.45	0.78	0.58
40	75,700	6.1	282,000	21.8	3.7	0.53	0.97	0.55

[a] Measured by SEC viscometry.
[b] Calculated using the Mark-Houwink equation $[\eta] = KM^a$.
[c] $g' = [\eta]_{hyper}/[\eta]_{linear}$.

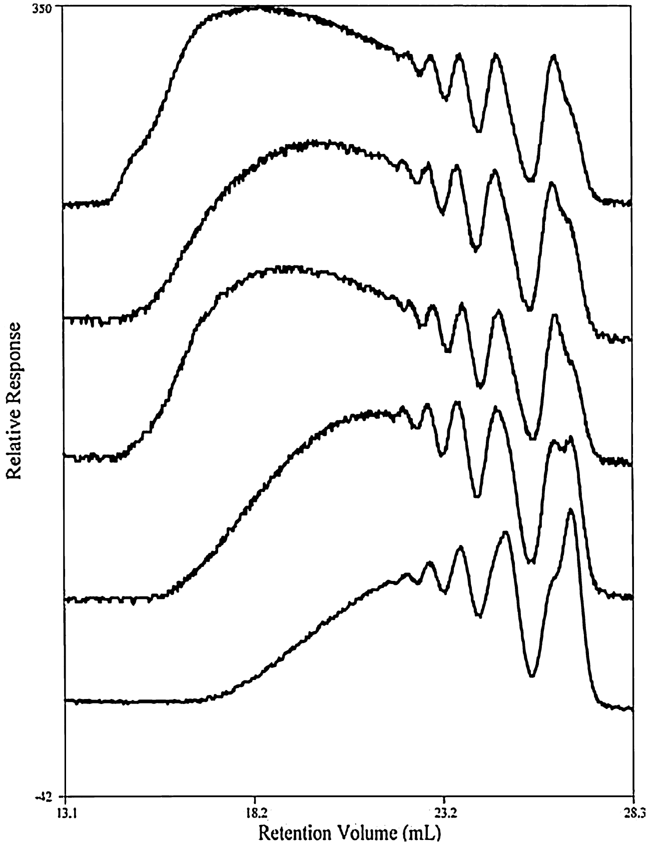


Figure 4.
SEC (RI detector) chromatograms (using 3 × 300 ml PLgel 5 μ 10^4 Å high resolution columns) showing influence of solution concentration w/v on extent of polycondensation and degree of cyclization. As the concentration of solution increases from 5% (bottom) to 40% (top) the extent of polycondensation increases and the degree of cyclization decreases.

volumes indicating the presence of cyclized dimer whereas at 40% the peak looks more skewed to lower retention volumes. However as alluded to above we feel that the ratio of intra to intermolecular reaction is not the only factor controlling the extent of reaction. Clearly, even at 40% solution concentration there is still a significant amount of uncoupled macromonomer, dimer and trimer, probably arising as a result of reaction between the alkyl chloride functionality and impurities in the DMF.

Although (as expected) the effect of this side reaction is reduced as the relative amount of DMF is reduced in the more concentrated solutions, it is not eradicated. Furthermore, as expected, an increase in the extent of reaction results in the value of g′, the branching factor, decreasing; from 0.68 for the most dilute solution to 0.55 for the most concentrated solution, indicating a higher degree of polycondensation and an increasingly compact, branched structure.

Conclusion

In this paper we describe a new strategy and synthetic route to synthesize polymers with a highly branched architecture by the polycondensation of AB_2 macromonomers with molecular weights in a range from 3,600 to 94,000 $gmol^{-1}$. Solution viscometry data obtained by size exclusion chromatography analysis of the resulting materials revealed that the products have a branched structure as indicated by branching factors, g', of 0.53–0.67 depending on the molecular weight of the macromonomer. The extent of the polycondensation reaction appears to be limited to a certain degree by two factors; the ratio of intramolecular to intermolecular reaction and by the likelihood of side reactions with impurities generated by heating the solvent, DMF, to reflux. It was found that the solution concentration has a great influence on the impact of these two limiting factors. At low solution concentrations, 5% w/v, the polycondensation reaction produced materials which were significantly lower in molecular weight, polydispersity and degree of branching than materials produced in a solution concentration of 40% w/v. Again the degree of intramolecular reaction is clearly demonstrated by SEC analysis.

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