

HyperMacs – Long Chain Hyperbranched Polymers. A Dramatically Improved Synthesis and Qualitative Rheological Analysis

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Abstract. We have previously reported a novel (albeit modestly successful) strategy for the synthesis of polystyrene HyperMacs - long chain branched analogues of hyperbranched polymers. The building blocks for HyperMacs, AB₂ macromonomers are synthesized by living anionic polymerization and as such are well-defined in terms of molecular weight and polydispersity but the nature of the coupling reaction used to generate the highly branched HyperMacs results in branched polymers with a distribution of molecular weights and architectures. In our previously reported studies the extent of the coupling reaction was significantly hampered by side reactions, however, we report here dramatic improvements to the coupling chemistry which overcome the previously experienced limitations resulting in a four fold increase in the extent of the coupling reactions. Furthermore we report the effect of the addition of varying amounts of a B₃ core molecule to the coupling reaction and the resultant ‘control’ of the final molecular weight of the HyperMac. Melt rheology showed polystyrene HyperMacs to be thermorheologically simple, obeying William-Landel-Ferry (WLF) behaviour. HyperMacs showed little evidence for relaxation by reptation and when the molecular weight of the macromonomer was $\leq M_e$ for polystyrene, HyperMacs resemble unentangled polymers below the gel point, despite being well above the entanglement molecular weight for linear polystyrene. Increasing the molecular weight of the macromonomer to substantially above M_e seems to introduce some entangled nature to the HyperMac as evidenced by the emergence of a near horizontal plateau in G'' - the loss modulus.

1. Introduction. The characterisation of the rheological properties of long-chain branched polymers has been an area of active research in both academia and industry for many years and structure-

property correlation studies have established that the presence of long-chain branching in polymers has a significant impact on the properties of such materials in the melt [1]. However, in the overwhelming majority of cases, industrially produced materials have a wide distribution of chain lengths between branch points, making modelling of the material challenging. It is this realisation that has, over a period of decades, resulted in the design and synthesis of well-defined molecular architectures such as star branched polymers [2,3], mikto star polymers [4-6] and H-shaped polymers [7,8] with a view to understanding and predicting the relationship between structure and properties. More recently, syntheses of dendrigraft, dendritically branched and arborescent [9-14] polymers with a higher degree and complexity of branching have been published, much of this work has recently been reviewed by Gauthier and Teertstra [15]. One of the earliest investigations into the synthesis [16] and characterisation of the rheological properties [17] of arborescent type polymers are reported by Gauthier et al. who studied the viscoelastic behaviour of these materials with increasing generations (increased levels of hierarchical branching). The results demonstrate that these branched polystyrene architectures have low zero-shear viscosities when compared to linear polystyrene of the same molecular weight. Knauss synthesised [10-12] and examined the melt rheology [18] of dendritically branched polystyrene and observed that these randomly branched polystyrenes with molecular weights above $1.0 \times 10^6 \text{ g mol}^{-1}$ exhibit high melt elasticity, but show little evidence of entanglement. However, in both these described architectures the synthetic strategies offer little or no control over the molecular weight between branch points.

The concept of macromonomers, monomers that are macromolecular species containing polymerizable end groups, was first described by Milkovich [19] who synthesised end functionalized polymers by living anionic polymerisation. Methods for the synthesis of highly branched polymer architectures using macromonomers as building blocks have subsequently been reported by a number of research groups including graft copolymers [20] and combs/star combs [21]. The advantage of the macromonomer approach in these strategies is the ability to control the

molecular weight of the branches/combs independently from the backbone although there is still a certain lack of control in the molecular weight between branch points. The optimal long chain branched polymer architecture for structure property correlation studies will have multiple generations of hierarchical branching in which not only is the molecular weight of each linear segment well defined but the position of each branch is also well controlled. These structures might be described as long chain branched analogues of dendrimers and the synthesis of such structures have been reported, notably by Hadjichristidis [22], Gnanou [9,23], Hedrick [24], Hirao [25,26], ourselves [27] and recently reviewed [28]. However in each case without exception the synthesis is time consuming involves multiple reaction steps and yields modest amounts of material.

We have also previously described the synthesis of HyperMacs [29] in a simple one-pot reaction involving the polycondensation of well defined AB_2 macromonomers prepared by anionic polymerisation. HyperMacs might be considered to be long chain branched analogues of hyperbranched polymers and as such can be produced in useful quantities. In the past decade it has been shown that the rheology of polymer melts may be tailored by controlled addition of long-chain branches using "open-site" metallocene catalysts [30] and although HyperMacs are not perfectly branched, one intriguing possible application of HyperMacs is as "model" systems for polymers prepared via the molecular mechanism of (metallocene catalysed) vinyl-group reincorporation which leads statistically to the same one-parameter topological family of branched structures [31] as the " AB_2 " polycondensation described for the synthesis of HyperMacs [29] - the only difference lying in the exponential polydispersity of the molecular weight between branches in the case of the metallocene catalysed system. A model system intermediate between the doubly-random ensemble of the metallocene catalysed polymers and perfectly branched molecules (such as monodisperse combs and dendritically branched polymers) would be a powerful tool in developing predictive approaches to melt rheology.

We previously reported that the coupling reaction used to create HyperMacs – a Williamson coupling reaction between an alkyl chloride ‘A’ functionality and phenol ‘B’ functionalities using potassium carbonate as the base in refluxing dimethylformamide (DMF) with 18-crown-6-ether as a phase transfer agent – was successful but that the extent of the coupling reaction was severely hampered by what we believed to be side reactions between the macromonomer and impurities arising from the degradation of DMF at elevated temperatures. We report here how we have improved the coupling strategy to overcome these limitations resulting in a fourfold increase in the extent of reaction. Furthermore, we report the effect of the addition of varying amounts of a B₃ core molecule to the coupling reaction and how we are now able to exert some degree over the control of the final molecular weight of the HyperMac – albeit whilst accepting that the resultant HyperMacs are still polydisperse with respect to both molecular weight and molecular architecture. We also report the results of some qualitative analytical investigations into the rheology of some examples of HyperMacs prepared during the original studies.

Experimental Section

Characterisation

Molecular weight analysis was carried out by size exclusion chromatography (SEC) on a Viscotek TDA 302 with refractive index, viscosity and light scattering detector (with a 690 nm wavelength laser). A value of 0.185 mL/g (obtained from Viscotek) was used for the dn/dc of polystyrene. 2 x 300 mm PLgel 5 μ m mixed C columns (with a linear range of molecular weight from 200-2,000,000 g mol⁻¹) were employed; Tetrahydrofuran (THF) was used as the eluent with a flow rate of 1.0 ml/min at a temperature of 30 °C. ¹H-NMR analysis was carried out on either a Varian Inova-500 MHz or Mercury-400 MHz spectrometer using C₆D₆ as a solvent. Spectra were referenced to the trace of C₆H₆ (7.2 ppm) present in the C₆D₆.

Void free sample disks of 1mm thick and 25mm or 8mm diameter were prepared by the use of a heated press and stainless steel moulds. The processing temperature was 443K and an inert

atmosphere of nitrogen was applied to minimize degradation. Rheology measurements were performed on Rheometrics SR5 and TA Instruments AR 2000 rheometers with parallel plate geometry, using an environmental test chamber (ETC). Linear rheology experiments were run over a temperature range of 383 – 463 K under an atmosphere of nitrogen and gap corrections made for plate expansion/contraction. Frequency sweeps in the range of 10^{-2} – 5×10^2 rad/s were performed in the temperature range at 10 K intervals and the data sets combined to form master curves by the time-temperature superposition principle.

Materials

The synthesis of AB₂ polystyrene macromonomers where A is an alkyl chloride group is described elsewhere [29]. Dichloromethane and benzene (both HPLC grade, Aldrich) were dried and degassed by stirring over calcium hydride powder (97%, Aldrich) and performing a series of freeze - pump-thaw cycles. Carbon tetrabromide (99%, Aldrich), cesium carbonate (99.995%, Aldrich), triphenylphosphine (99%, Aldrich), dimethylformamide (99.9+%, Aldrich) and 1,1,1-tris(4-hydroxyphenyl)ethane (Aldrich) were all used as received.

Synthesis of AB₂ Polystyrene Macromonomers. The synthesis of polystyrene macromonomers in which the reactive ‘A’ functionality is an alkyl chloride is described previously [29]. The final step in this process is the halogenation of a primary alcohol group which was introduced as a protected functionality on the lithium initiator used in the anionic polymerization of styrene. In the present study we have investigated the effectiveness of bromine as a alternative leaving group.

Bromination of primary alcohol group. In a 1 litre round bottom flask, 50 grams of the AB₂ macromonomer (A = OH) ($28,000 \text{ g mol}^{-1}$, $1.78 \times 10^{-3} \text{ mol}$), and triphenylphosphine (1.0g, 3.56×10^{-3}) was dissolved in 500ml of dried dichloromethane under an inert atmosphere of nitrogen. The macromonomer solution was cooled in an ice/water bath and carbon tetrabromide (1.5g, $4.45 \times 10^{-3} \text{ mol}$) added. The mixture was stirred at room temperature and the progress of the reaction followed by ¹H-NMR (in C₆D₆) until (24 hours) the signal for the CH₂-OH (3.26 ppm) had been completely

replaced by a new signal for CH₂-Br at 2.75 ppm. The polymer was recovered in quantitative yield by precipitation into methanol, redissolved and reprecipitated once more, collected by filtration and dried to constant mass in vacuo.

HyperMac synthesis. Coupling reactions were carried out under an inert atmosphere of either argon or nitrogen. Although the reaction temperature, leaving group and base were parameters that were investigated, a typical Williamson coupling reaction was carried out thus, 2 g of macromonomer (M_n 28,000 g mol⁻¹, 7.14×10^{-5} mol) and 0.26 g (7.14×10^{-4} mol) cesium carbonate were dissolved in 10 ml of DMF. The solution was raised to the desired temperature 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. 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.

HyperMac synthesis in the presence of a B₃ core molecule. Coupling reactions were carried out as described above except for the presence of 5 and 10 mol % (with respect to macromonomer) of 1,1,1-tris(4-hydroxyphenyl)ethane – a B₃ core molecule. The core molecule was added with the macromonomer at the start of the reaction.

Results and Discussion

Previously [29] we have reported a novel strategy for the synthesis of polystyrene HyperMacs - long chain branched analogues of hyperbranched polymers. The building blocks for HyperMacs, AB₂ macromonomers, are synthesized by living anionic polymerization, initiated by 3-*tert*-butyldimethylsiloxy-1-propyllithium which has a protected primary alcohol functionality. The living polystyryl lithium was quantitatively end-capped with 1,1-*bis*(4-*tert*-butyldimethylsiloxyphenyl)ethylene thereby introducing two protected phenol groups at the chain end. Deprotection of the protected alcohol groups via a mild acid hydrolysis and halogenation of the

primary alcohol group generates an AB₂ macromonomer which is well-defined in terms of molecular weight and polydispersity. These macromonomers can be coupled via a Williamson reaction to generate the highly branched HyperMacs - branched polymers with a distribution of molecular weights and architectures. Although this coupling strategy was successful, we reported that when the halogen leaving group is chlorine, the coupling reactions had to be carried out in refluxing DMF in order to generate the branched structures and that the extent of the coupling reaction was apparently hampered by side reactions with impurities generated by heating the solvent, DMF, to reflux. Under the standard reaction conditions (20% w/v macromonomer in refluxing DMF/K₂CO₃/18-crown-6) it was shown that polystyrene macromonomers with molecular weights (M_n) from 3,600 – 37,300 gmol⁻¹ underwent successful coupling reactions to yield branched polymers. We find it most convenient to describe the extent of the coupling reaction in terms of the degree of polymerization, D_p , where D_p describes how many macromonomers have reacted. Hence D_{p_n} equals $M_n(\text{HyperMac})/M_n(\text{Macromonomer})$ and D_{p_w} is $M_w(\text{HyperMac})/M_w(\text{Macromonomer})$. As AB₂ coupling reactions of this type proceed, M_w and therefore D_{p_w} increases more rapidly than M_n and therefore D_{p_n} . It can be seen from the data in Table 1 that these coupling reactions generate HyperMacs with values of D_{p_n} of 4.2 – 5.3 and values of D_{p_w} of 9.6 – 17.3. The relationship between molecular weight of macromonomer and extent of coupling reaction is discussed elsewhere [29]. The branching factor (g') is defined as the ratio of the intrinsic viscosity $[\eta]$ of a branched polymer to that of a linear polymer of the same molecular weight. Branched polymers in solution have smaller hydrodynamic volumes, are more compact than linear polymers of identical molecular weight and therefore have relatively lower intrinsic viscosities – hence g' for a branched polymer will be less than unity. Values of g' were obtained for each HyperMac (see Table 1) and the data lies within a reasonably narrow range (0.56-0.67) confirming that HyperMacs possess a branched structure. Furthermore these data compare very favorably with the data reported by Hirao *et al* [25] for well-defined, narrow polydispersity

dendrimer-like polymers who reported values for g' of 0.80, 0.59 and 0.46 for a first, second and third generation dendrimer-like polymethyl methacrylate. Whilst undoubtedly this previously described strategy works, the extent of the coupling reaction was modest and we have argued that the degradation of DMF at elevated temperatures is the chief cause.

We report here the results of our successful investigations to enhance the original strategy in order to overcome this problem. Our objective was to increase the rate of the coupling reaction such that we could carry out these reactions at lower temperatures – thereby avoiding the degradation of DMF. With this aim we considered two possible ways in which the Williamson reaction could be improved – either by changing the leaving group and/or changing the base.

Modified Williamson Coupling Reactions

We have synthesized an AB₂ polystyrene macromonomer (M_n 28,000 g mol⁻¹) in which the leaving group 'A' was bromine. The macromonomer synthesis was essentially identical to that described previously [29] for the synthesis of macromonomers with a chlorine leaving group except for the final step where the primary alcohol group is converted to bromine using carbon tetrabromide and triphenyl phosphine. In order to compare the relative reactivities of chlorine and bromine as leaving groups a large batch of macromonomer was synthesized and divided into two - one half was chlorinated and the other half brominated – thereby avoiding any dissimilarity in reactivity due to molecular weight. Subsequent coupling reactions were carried out in DMF at 100 °C with 20% w/v solutions of macromonomer. In the first instance potassium carbonate was used as the base to deprotonate the phenol groups and 18-crown-6-ether used as a phase transfer agent since potassium carbonate is insoluble in DMF.

Effect of Leaving Group

It can be seen from the data in Figure 1 that changing the leaving group from chlorine to bromine resulted in both an increase in the rate and extent of coupling reaction. At 100° C the chlorinated macromonomer (using potassium carbonate as the base) reacts very slowly. The extent of reaction,

shown as Dp_w (M_w HyperMac/ M_w macromonomer) increases steadily albeit very slowly to a value of Dp_w of about 4 after 7 hours. In previous studies analogous reactions carried at in refluxing DMF (c. 160°C) produced HyperMacs with Dp_w values of 10-17 (depending on molecular weight of macromonomer) in much shorter periods of time [29]. The brominated macromonomer of identical molecular weight showed a higher rate and extent of reaction under the same conditions. In Figure 1 it can be seen that the Dp_w rises up to a value of about 11 during the first hour followed by a more gentle increase up to 15.5 after 7 hours. Data collected after 24 hours (not shown on graph) indicated that the reaction was still proceeding during this period with a final value of Dp_w of a little over 17. Although replacing chlorine with bromine as the leaving group results in a marked increase in both the rate and extent of reaction the results obtained for the brominated macromonomer are not really an improvement over the previous work – albeit that the reactions were carried at temperatures which were 60° C lower.

Effect of Base.

In order to further improve the efficiency of these reactions it was decided to look at an alternative to potassium carbonate as the base. Although 18-crown-6-ether (18-C-6) had been employed as a phase transfer agent the poor solubility of potassium carbonate in DMF was considered to be a possible limitation. It has been described in the literature that cesium carbonate is a particularly efficient base for Williamson coupling reactions of this type in DMF due to the greater solubility of both cesium carbonate and the resulting phenolate [32]. To gauge the potential benefits of using cesium carbonate a coupling reaction was initially carried out on the chlorinated macromonomer and it can be seen (Figure 1) that cesium carbonate in the absence of any phase transfer agent notably outperformed potassium carbonate/18-C-6. The reaction was slow in the early stages and for the first two hours proceeded only slightly faster than the reaction with potassium carbonate but the rate then increased and values of Dp_w of approaching 8.5 were obtained after 7 hours – approximately double that obtained with potassium carbonate. Although the improvement was

notable it was not impressive. However, when cesium carbonate was used with the more efficient leaving group – bromine - the improvement in both the rate and extent of reaction was dramatic. After one hour the Dp_w had risen to nearly 60 after which there was little increase in Dp_w . The combined effect of bromine as a leaving group and cesium carbonate as the base far exceeded what we might have expected given the previous results and suggests a synergistic effect of these two modifications. Although we believe that after an initial very rapid increase in molecular weight the rate of increase of molecular weight does slow, it should be noted that the data shown in Figure 1 was obtained via SEC and that the samples collected for molecular weight analysis were almost gel like and had to be filtered before analyzing for fear of blocking the SEC columns. We don't believe that these very high molecular weight HyperMacs ($M_n \sim 400,000 \text{ g mol}^{-1}$, $M_w \sim 1.7 \text{ million g mol}^{-1}$) have formed insoluble crosslinked networks but we do believe that given their high polydispersity ($PDI \sim 4.0$) it is inevitable that there is a VERY high molecular weight component to these HyperMacs which results in this gel like behaviour (reluctance to dissolve) and that it is likely that filtration (0.2 micron filter) removes some of the highest molecular material from the SEC sample with a concomitant underestimation of the molecular weight by SEC.

Effect of Temperature

Given the dramatic increase in the efficiency of the Williamson coupling reactions and that the reactions appeared to be virtually complete within the first hour it was decided to see if these reactions could be carried out to the same extent but at lower temperatures. One benefit of slowing the reaction down such that it proceeds over several hours rather than less than one hour is the possibility to stop the reaction at any given conversion – thereby offering some control/predictability over the final molecular weight of the HyperMac. A series of otherwise identical coupling reactions were carried in which temperature was varied from 100°C to room temperature - the results are shown in Figure 2. Reducing the temperature from 100° C to 70° C made no significant difference to the rate of reaction however further reductions in temperature to

40° C, 30° C and eventually to room temperature (21° C) progressively slowed the rate of coupling. For reactions carried out 40° C and higher the overall extent of reaction is similar - with final values of Dp_w in the range 60-70. There clearly is some variation in the final values of Dp_w but we suspect that at these very high molecular weights, filtration of the solutions for SEC analysis introduces a degree of error in the accuracy of these data. As alluded to previously it is likely that the filtration of these samples removes some of the highest molecular weight fraction of the HyperMacs and we certainly don't believe that the molecular weights are dropping with time as suggested by the 70° C data. At 30° C and at room temperature it appears from Figure 2 that the reactions are slowed to the point that the reactions are incomplete within the times that they were followed - although the trend in Dp_w is still upward - suggesting that given longer reaction times the extent of reaction would continue to increase. Whilst we cannot be absolutely certain of the final extent of the coupling reactions, it is interesting to note that the reactions appear to proceed in three distinct phases – this is most evident in the data obtained at 40° C. During the first phase one can observe a steady increase in Dp_w (molecular weight) then after 1 – 2 hours the molecular weight begins to increase at a much higher rate; this second phase lasts for a relatively short period of time and is followed by a third and final phase in which the rate of increase in molecular weight slows down again suggesting that the rate of increase in molecular weight will plateau. We believe that during the first phase reaction occurs initially between individual macromonomers and then between macromonomers and HyperMacs comprising of only a few macromonomers. The onset of the rapid increase in molecular weight observed in phase two arises predominantly via the coupling of HyperMac to HyperMac eventually resulting in the presence of a significant proportion of very high molecular weight species. The emergence of these “super” HyperMacs towards the end of the second phase can be seen in the SEC chromatograms (figure 3). The SEC chromatogram recorded 90 minutes into the coupling reaction (figure 3a) indicates that there is still a significant amount of uncoupled macromonomer - as evidenced by the sharp peak with a retention volume of about 14.3 ml – as well

as well as dimer and trimer with peaks at 13.7 ml and 13.2 ml respectively. From the data shown in figure 2 for this reaction we can see that after 90 minutes the reaction is just entering the second phase where the rate of increase in molecular weight starts to increase dramatically. The SEC chromatogram obtained after 2 hours (figure 3b) shows the molecular weight distribution as the reaction is well into the second phase. It can be seen that the relative intensity of the peak at 14.3 ml has diminished indicating further macromonomer has been consumed and the main broad peak maximum has shifted from 12.2 ml to 11.5 ml indicating an increase in molecular weight. Furthermore, the emergence of a shoulder to lower elution volumes (between 10 and 10.5 ml) can be observed which we propose arises as a result of the coupling of HyperMac to HyperMac. This emerging shoulder becomes more pronounced with time and after 4 hours (figure 3c) the relative intensity of this shoulder is greater than that of the macromonomer peak at 14.2 ml indicating the presence of a significant proportion of the very high molecular weight “super” HyperMacs. The data in figure 2 suggests that after 4 hours the coupling reaction is into the final phase where the high molecular weight leads to very high solution viscosities making efficient stirring/mixing a limitation. It is likely that reaction of the diminishing number of reactive ‘A’ functionalities becomes diffusion controlled and the rate of reaction drops resulting in the plateau that defines the third phase of the coupling reaction.

To demonstrate that these HyperMacs have a highly 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 $[\eta]_{\text{hyper}}$ to the intrinsic viscosity of a linear polymer $[\eta]_{\text{linear}}$ of the same molecular weight [25,33]. Shown in Table 2 is data obtained for the HyperMac coupling reaction carried out in DMF, with cesium carbonate, at 40°C with the brominated macromonomer and shows the development of intrinsic viscosity of the HyperMac, $[\eta]_{\text{hyper}}$, with time and the intrinsic viscosity of a series of linear polymers of the same M_w . The intrinsic viscosity of the linear polymers was calculated using the Mark-Houwink equation with

vales of $a = 0.712$ and $K = 12.8 \times 10^{-5} \text{ dl/g}$ (supplied by American Polymer Standards Corporation). As the molecular weight of the HyperMac increases, so does the intrinsic viscosity, but at a much slower rate than would be expected for a linear polymer of identical molecular weight. This is to be expected if the resulting polymers have a branched architecture since branched polymers have smaller hydrodynamic volumes and are more compact than linear polymers of identical molecular weight, they therefore have relatively lower intrinsic viscosities. As the reaction proceeds the values of $[\eta]_{\text{hyper}}$ and $[\eta]_{\text{linear}}$ diverge and the value of g' decreases indicating increasingly compact, branched structures. 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. Despite that caveat, the values of g' – as low as 0.35 – undoubtedly confirms that this HyperMac is very highly branched and furthermore the values of g' are considerably lower than those observed for HyperMacs prepared by the original methodology [29] which had much lower values of Dp_n and Dp_w and g' values of between 0.7 and 0.55 (table 1). This is not unexpected given the dramatic improvements seen in the extent of reaction of the coupling reactions.

Effect of the addition of B_3 core molecule to the coupling reaction.

It is well established that coupling reactions of AB_2 monomers in the presence of a B_n core molecule can result in significant changes in the properties of the resultant materials. Feast and Hobson carried out a series of AB_2/B_n ($n = 2-6$) copolymerizations to make poly(amidoamine) hyperbranched polymers [34]. They observed that the addition of such core (B_n) molecules lead to a reduction in the molecular weight and that by varying either the functionality of B_n or the molar ratio of core to monomer – a degree of control over the molecular weight of the resultant polymers was possible. They further postulated that addition of B_n core molecules could provide a single step

route to produce pseudo-dendrimers. Analogous conclusions were drawn by Malmström and Hult [35] about the ability of B_n polyol cores to modify and ‘control’ the formation of hyperbranched polyesters based on 2,2-bis(methylol)propionic acid. In light of these observations and in an attempt to gain further control over the synthesis of HyperMacs a series of coupling reactions were carried with an AB_2 macromonomer (M_n 28,000 g mol^{-1}) in the presence of 1,1,1-tris(4-hydroxyphenyl)ethane, a trifunctional B_3 core molecule. The B_3 core was present at three different levels, 0, 0.05 and 0.10 molar with respect to the amount of macromonomer. It can be seen very clearly from figure 4 that as the level of B_3 increases, the molecular weight of the resulting HyperMac decreases such that in the absence of any core the Dp_n and Dp_w are 18 and 54 respectively whereas an identical reaction carried out in the presence of 10 mole percent of core (with respect to moles of AB_2 macromonomer) yielded a polymer with a Dp_n of 4.5 and a Dp_w of 21.

Rheology

Qualitative rheological analysis was carried out on three samples of HyperMac prepared by the ‘original’ synthetic methodology. The HyperMacs in question had macromonomers with molecular weights below (HM 1), approximately equal to (HM 2) and above (HM 3) the entanglement molecular weight for polystyrene [36] see Table 3. Linear rheology measurements demonstrate that HyperMacs obey time-temperature superposition with the vertical shifts in the moduli response being negligible. The William-Landau-Ferry expression $\log(a_T) = -C_0(T - T_{ref}) / (C_1 + T - T_{ref})$ [37] was used to fit master curves and shift values are: $C_0 = 3.5 \pm 0.2$ K and $C_1 = 81.1 \pm 15.0$ K which, within experimental error, closely match previously reported values for a series of star branched polystyrenes [38]. Figure 5 shows the storage (G') and loss (G'') moduli curves for the three HyperMacs with different molecular weight macromonomers and the variation between the samples is worth noting. Theory predicts that at high frequencies, G' for polydisperse randomly branched polymers should have a slope of approximately 0.66 at the gel point [39] – Figure 5

confirms that in the case of all three HyperMacs, the storage modulus versus frequency at frequencies above 1000 rad s^{-1} varies accordingly suggesting the onset of gel like behaviour. Interestingly, in the case of HM 1 and HM 2, the absence of a true rubbery plateau suggests that these materials are essentially unentangled despite having molecular weights significantly above M_e for linear polystyrene. M_n (HM 1) is approximately $3M_e$ and M_n (HM 2) is approximately $6M_e$. This is consistent with the work of Knauss *et. al.* [11,18] who reported a similar behaviour for hyperbranched polystyrenes with M_w in excess of 10^6 gmol^{-1} . Clearly the apparent absence of entanglements is the result of the highly branched architecture. However in the case of HM 3 in which the molecular weight of the macromonomer is close to $100,000 \text{ gmol}^{-1}$ the slope of G'' – the loss modulus – is much more shallow than in the case of HM 1 and HM 2, indicating the presence of some chain entanglement. Furthermore, for HM 3, in contrast to HM 1 and HM 2, across the entire frequency range the storage modulus is greater than the loss modulus, which is also indicative of an entangled viscoelastic regime. Since we were not able to observe a low frequency crossover between G' and G'' , the longest relaxation time must be greater than 10^3 s . It is also worth noting that the magnitude of the storage modulus is comparable to that. It is apparent that it is possible to prepare high molecular weight polymers which are essentially unentangled provided that the molecular weight of the linear segments between branch points is significantly above M_e . A more detailed quantitative analysis of the rheology HyperMacs is not possible because of their high polydispersity however separation of HM 2 into a number of less polydisperse fractions has been carried out and a detailed discussion of the rheology reported elsewhere [40].

Conclusions We have shown that the synthesis of polystyrene HyperMacs can be dramatically improved by the use of bromine (instead of chlorine) as a leaving group on the macromonomer and by the use of cesium carbonate (instead of potassium carbonate) as the base in the Williamson coupling reaction. The combined effect of these two modifications results in increases in the extent of coupling reaction far in excess of that which might be expected from experiments in which each

modification was investigated in isolation. There appears to be a synergistic benefit in using Br/Cs₂CO₃ in combination. The huge increase in the rate of the coupling reactions has allowed us to reduce the reaction temperature from 160° C to room temperature although the optimum temperature would appear to be 40° C. At these significantly lower temperatures, the degradation of DMF - which so inhibited the less efficient coupling reactions as previously reported – no longer appears to be a limiting factor. Whilst it is clearly understood that because of the nature of the coupling reaction, it is inevitable that HyperMacs will be polydisperse both in terms of molecular weight and molecular architecture, we have demonstrated that using well defined macromonomers we can control the molecular weight between branch points and vary the total molecular weight of the HyperMac and we have demonstrated that at 40°C the rate of reaction is such that in theory the reaction could be stopped at a chosen conversion – again offering some control over the final molecular weight. Furthermore we have commented on the effect of the molecular weight of the macromonomer on the rheological properties – namely that only when the molecular weight of the linear segments is significantly above the entanglement molecular weight of polystyrene do we see any evidence of chain entanglement.

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Figure 1 The effect of macromonomer leaving group and base on the extent of Williamson coupling reaction (DMF/100° C) used to prepare HyperMacs from polystyrene AB₂ macromonomer M_n 28,000 g mol⁻¹

Figure 2. The effect of temperature on the extent of Williamson coupling reaction used to prepare HyperMacs from polystyrene AB₂ macromonomer M_n 28,000 g mol⁻¹

Figure 3. SEC chromatograms (RI trace) of HyperMac coupling reaction carried out at 40° C for a) 90 minutes, b) 120 minutes and c) 240 minutes

Figure 4. Effect of the addition of B₃ core on the extent of Williamson coupling reaction (Dp_n and Dp_w) used to prepare HyperMacs from polystyrene AB₂ macromonomer M_n 28,000 g mol⁻¹. Reaction carried out brominated macromonomer, at room temperature for 24 hours with Cs₂CO₃.

Figure 5. Storage (G' – filled symbols) and loss (G'' – open symbols) moduli of HyperMacs synthesised from various macromonomers (see Table 3). □/■ = HM 1, ○/● = HM 2, △/▲ = HM 3) (T₀ = 150 °C)

Table 1. Molecular weight, polydispersity and intrinsic viscosity data for HyperMacs synthesized from AB₂ macromonomers where ‘A’ is chlorine

Macromonomer	M _n /gmol ⁻¹	Dp _n	M _w /gmol ⁻¹	Dp _w	PDI	[η] _{hyper} /dlg ^{-1a}	[η] _{lin} /dlg ^{-1b}	g ^c
3,600 gmol ⁻¹	16,100	4.5	36,600	9.6	2.2	0.15	0.23	0.65
6,300 gmol ⁻¹	33,600	5.3	65,400	10.1	1.9	0.23	0.34	0.67
12,400 gmol ⁻¹	52,600	4.2	167,000	13.0	3.2	0.42	0.67	0.63
16,800 gmol ⁻¹	88,000	5.2	298,000	17.3	3.4	0.57	1.01	0.56
37,300 gmol ⁻¹	185,000	5.0	556,000	14.3	3.0	0.94	1.58	0.59

^a Measured by SEC viscometry.

^b Calculated using the Mark-Houwink equation $[\eta] = KM^a$.

^c $g' = [\eta]_{\text{hyper}}/[\eta]_{\text{linear}}$.

Table 2. Molecular weight, polydispersity and intrinsic viscosity data for HyperMac synthesised from an AB_s macromonomer where ‘A’ is bromine. Coupling reaction carried out in DMF, at 40° C with Cs₂CO₃.

Time/hours	M _n /gmol ⁻¹	M _w /gmol ⁻¹	PDI	[η] _{hyper} /dlg ^{-1a}	[η] _{lin} /dlg ^{-1b}	g ^c
0	28,000	28,600	1.02	-	-	-
0.5	61,300	103,300	1.7	0.39	0.48	0.81
1	109,400	231,400	2.1	0.55	0.84	0.65
1.5	161,800	483,900	3.0	0.79	1.43	0.56
2	296,700	1,406,000	3.5	1.04	2.47	0.42
2.5	419,800	1,465,000	3.5	1.20	3.14	0.38
3	462,400	1,774,000	3.8	1.27	3.60	0.35
4	473,400	1,756,000	3.7	1.26	3.57	0.35
5	496,200	1,877,000	3.8	1.30	3.75	0.35
6	471,100	1,792,000	3.8	1.31	3.63	0.36
8.5	525,100	1,790,000	3.4	1.30	3.62	0.36

^a Measured by SEC viscometry.

^b Calculated using the Mark-Houwink equation $[\eta] = KM^a$.

^c $g' = [\eta]_{\text{hyper}}/[\eta]_{\text{linear}}$.

Table 3. Molecular weight and polydispersity data for HyperMacs used in rheological studies

Sample	Macromonomer			HyperMac		
	M_n/gmol^{-1}	M_w/gmol^{-1}	PDI	M_n/gmol^{-1}	M_w/gmol^{-1}	PDI
HM 1	6,200	6,500	1.05	43,700	91,000	2.10
HM 2	16,100	16,400	1.02	91,800	226,700	2.46
HM 3	93,900	104,200	1.11	324,500	682,800	2.10