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HyperMacs – Highly Branched Network Precursors or Semi-Interpenetrating Networks?

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Summary: We describe here a strategy for the synthesis of HyperMacs – long-chain branched analogues of hyperbranched polymers. The building blocks for HyperMacs, AB_2 macromonomers, are synthesized by living anionic polymerization and, as such, are well-defined in terms of molecular weight (MW) and polydispersity. Size exclusion chromatography (SEC) studies show that the nature of the coupling reaction used to generate the highly branched HyperMacs results in branched polymers with a distribution of MWs and architectures. Solubility studies show that, in certain cases, a significant weight fraction of the resulting HyperMacs forms insoluble, swollen gels when added to a good solvent, and SEC analysis shows that a modest weight fraction of the soluble polymer has a "very high MW", in excess of 10,000,000 $g\,mol^{-1}$. Although an AB_2 coupling reaction should, in theory, not lead to a "crosslinked" network, such is the efficiency of this reaction that the resulting polymers appear to behave as semi-interpenetrating networks.

Keywords: anionic polymerization; branched; HyperMacs; networks

Introduction

It has long been understood that the physical properties of polymeric materials depend, to a very large extent, on the molecular architecture of the constituent polymer chains. Variables such as molecular weight (MW), polydispersity and the presence and degree of branching/crosslinking in polymers have huge implications not only for the final solid state properties of a product but also for properties in the melt and, of course, these parameters strongly impact upon rheology and processing. The characterization of the relationship between the molecular structure and physical properties of long-chain branched polymers has been an area of active research in both academia and industry for many years.[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 materials challenging. It is this realization 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-arm 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, strategies have been devised to synthesize yet more complex, hierarchically, branched architectures with various resulting structures and differing degrees of control over molecular structure. Reports describing the synthesis of dendrigraft, arborescent, dendritic and hyperbranched[9–16] polymers with a higher degree and complexity of branching have been published; much of this work has recently been reviewed by Gauthier and Teertstra.[17] However, in the majority of these described architectures, the synthetic strategies offer little or no control over the MW between branch points.

The concept of macromonomers – monomers that are macromolecular species containing polymerizable end-groups – was

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first described by Milkovich[18] who synthesized end-functionalized polymers by living anionic polymerization. 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[19] and combs/star combs.[20] The advantage of the macromonomer approach in these strategies is the ability to control the MW of the branches/combs independently from the backbone, although there is still a certain lack of control in the MW between branch points.

The optimal long-chain branched polymer architecture for structure-property correlation studies should have multiple generations of hierarchical branching, in which, not only is the MW of each linear segment well-defined, but the position of each branch is also controlled. These structures might be described as long-chain branched analogues of dendrimers and the synthesis of such structures has been reported, notably by Hadjichristidis,[21] Gnanou,[9,22,23] Hedrick,[24] Hirao,[25,26] ourselves[27,28] and recently reviewed.[29,30] However, in each case, without exception, the synthesis is time consuming, involving multiple reaction steps and yielding modest amounts of material.

It is also desirable that in the study of polymer networks and their properties, a certain amount of control during the synthesis should limit the heterogeneity in the structure of the final network. The use of living and controlled polymerization techniques to prepare network precursors, such as end-functionalized macromonomers[31,32] and well-defined star-branched polymers,[33,34] have been described. Such strategies aim to offer a degree of control over MW between crosslinks and the functionality of the crosslinks, i.e. the number of linear segments emanating from a crosslink, and this approach is helpful in understanding the relationship between the structure and properties of the network.

We have previously described the synthesis of HyperMacs[35] in a simple one-pot reaction involving the polycondensation of well defined AB_2 macromonomers prepared by anionic polymerization. HyperMacs might be considered long-chain branched analogues of hyperbranched polymers and, as such, can be produced easily in useful quantities. Initially, we reported that the coupling reaction used to create HyperMacs – a Williamson coupling reaction between an alkyl chloride 'A' functionality and phenol 'B' functionalities, using K_2CO_3 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 believe to be side reactions between the macromonomer and impurities arising from the degradation of DMF at elevated temperatures.[35] We have more recently modified and improved the coupling reaction to overcome these limitations, resulting in, at least, a fourfold increase in the extent of the reaction. The resulting HyperMacs have very high MWs with M_n *ca.* 500 kg mol^{-1} and M_w approaching 2,000 kg mol^{-1}. Furthermore, recent examination of the size exclusion data shows that these HyperMacs contain a modest but significant weight fraction with molar masses that are estimated to be in the tens of millions of g mol^{-1}. Solubility studies on these HyperMacs have revealed that the size exclusion chromatography (SEC) data only tell part of the story and reveal that there is an insoluble gel fraction which suggests that these high MW HyperMacs are in fact semi-interpenetrating networks.

Experimental Part

Characterization

MW analysis was carried out by SEC on a Viscotek TDA 302 with refractive index, viscosity and right-angle laser light scattering (RALLS) detector (with a 690 nm wavelength laser). A value of 0.185 mL g^{-1} (obtained from Viscotek) was used for the d*n*/d*c* of polystyrene. 2 × 300 mm PLgel

5 μm mixed C columns (with a linear range of MW 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^{-1} at a temperature of 35 °C. ^{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 C_6D_6.

Materials

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) and dimethylformamide (99.9 + %, Aldrich) were all used as received.

Synthesis of AB$_2$ Polystyrene Macromonomers

The synthesis of AB_2 polystyrene macromonomers where A is an alkyl chloride group is described elsewhere.[35] 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 used macromonomers functionalized with bromine as an alternative leaving group.

Bromination of primary alcohol group

In a 1 L round-bottom flask, 50 g of the AB_2 macromonomer (A = OH) (28,000 g mol^{-1}, 1.78×10^{-3} mol), and triphenylphosphine (1.0 g, 3.56×10^{-3} mol) was dissolved in 500 mL of dried dichloromethane under an inert atmosphere of nitrogen. The macromonomer solution was cooled in an ice/water bath and carbon tetrabromide (1.5 g, 4.45×10^{-3} mol) was added. The mixture was stirred at room temperature and the progress of the reaction was followed by ^{1}H-NMR (in C_6D_6) until (24 hours) the signal for the CH_2-OH (3.26 ppm) was completely replaced by a new signal for CH_2-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. A typical Williamson coupling reaction was carried out. Thus, 2 g of halogenated 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 was stirred vigorously. The progress of the coupling reaction was followed by extracting small samples periodically and subjecting the sample to SEC analysis. The reaction was deemed to be complete when no further increase in MW 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*.

Results and Discussion

Synthesis

Previously[35] we have reported a novel strategy for the synthesis of polystyrene HyperMacs - long chain branched analogues of hyperbranched polymers. The building blocks for HyperMacs, AB_2 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 followed by halogenation of the primary alcohol group generates an AB_2

macromonomer which is well-defined in terms of MW and polydispersity. These macromonomers can be coupled via a Williamson reaction to generate the highly-branched HyperMacs - branched polymers with a distribution of MWs 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/K_2CO_3/18-crown-6), it was shown that polystyrene macromonomers with M_n from 3,600–37,300 g mol^{-1} underwent (modestly) 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, DP, where DP describes how many macromonomers have reacted. Hence DP_n is M_n(HyperMac)/M_n(Macromonomer) and M_w(HyperMac)/M_w(Macromonomer) gives DP_w. These coupling reactions gave HyperMacs with values of DP_n (4.2–5.3) and DP_w (9.6–17.3). While, undoubtedly, this initial 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 have subsequently modified this 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 have considered two possible ways in which the Williamson reaction could be improved – either by changing the leaving group and/or changing the base. We therefore synthesized an AB_2 polystyrene macromonomer (M_n 28,000 g mol^{-1}) in which the leaving group 'A' was bromine. 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 MW. Subsequent coupling reactions were carried out in DMF at 100 °C with 20% w/v solutions of macromonomer. In the first instance K_2CO_3 was used as the base to deprotonate the phenol groups and 18-crown-6-ether used as a phase transfer agent since K_2CO_3 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 K_2CO_3 as the base) reacts very slowly. The extent of reaction, shown as DP_w increases steadily, albeit very slowly to a value of DP_w of about 4 after 7 hours. In previous studies, analogous reactions carried out in refluxing DMF (ca. 160 °C) produced HyperMacs with DP_w values of 10–17 (depending on the MW of macromonomer) in much shorter periods of time. The brominated macromonomer of identical MW showed a higher rate and extent of reaction than the chlorinated macromonomer under the same conditions. Figure 1 shows that 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 the 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

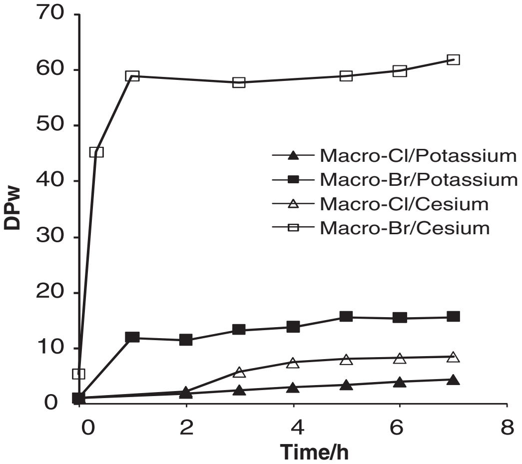

Figure 1.
The effect of macromonomer leaving group and base on the extent of Williamson coupling reaction (DMF/100 °C) used to prepare HyperMacs from polystyrene AB_2 macromonomer of M_n 28,000 g mol^{-1}.

alternative to K_2CO_3 as the base. It has been described in the literature that cesium carbonate (Cs_2CO_3) is a particularly efficient base for Williamson coupling reactions of this type in DMF due to the greater solubility of both Cs_2CO_3 and the resulting phenolate.[36] To gauge the potential benefits of using Cs_2CO_3, a coupling reaction was initially carried out on the chlorinated macromonomer and it can be seen from Figure 1 that Cs_2CO_3 in the absence of any phase transfer agent notably outperformed K_2CO_3/18-C-6. The reaction was slow in the early stages and, for the first 2 hours, it proceeded only slightly faster than the reaction with K_2CO_3, but the rate then increased and values of DP_w of approaching 8.5 were obtained after 7 hours – approximately double that obtained with K_2CO_3. Although the improvement was notable, it was not impressive. However, when Cs_2CO_3 was used in conjunction with bromine, the improvement in both the rate and extent of reaction was dramatic. After 1 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 Cs_2CO_3 as the base far exceeded what might have been 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 MW, the rate of increase of MW does slow, it should be noted that the data shown in Figure 1 were obtained via SEC and that the samples collected for MW analysis were almost gel-like and had to be filtered before analyzing for fear of blocking the SEC columns. We do not believe that these very high MW HyperMacs have or indeed could form insoluble crosslinked networks but we do believe that, given their high polydispersity index (PDI ~ 4.0), it is inevitable that there is a significantly high MW component to these HyperMacs which results in this gel-like behavior. The dramatic improvement in the efficiency of the coupling reactions allowed the reaction temperature to be further reduced to 40 °C without any reduction in the extent of reaction (Figure 2). However, at 40 °C the rate of reaction was slowed sufficiently to allow samples to be extracted for analysis and the progress of the reaction to be followed by SEC.

Size Exclusion Chromatography (SEC) Analysis

While we cannot be absolutely certain of the final extent of the coupling reactions due to the partial gel formation, it is

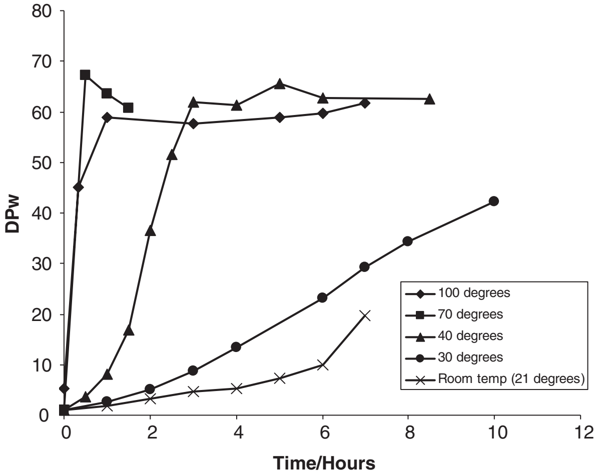

Figure 2.
Effect of temperature on the extent of Williamson coupling reaction used to prepare HyperMacs from polystyrene AB_2 macromonomer of M_n 28,000 g mol^{-1}.

interesting to note that the reactions appear to proceed in three distinct phases – this is most evident in the data obtained with Cs_2CO_3 as base at 40 °C (Figure 2 and Table 1).

During the first phase, one can observe a steady increase in DP_w (and MW). Then, after 1½ hours, the MW 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 MW slows down again, suggesting that the rate of increase in MW will plateau. We believe that, during the first phase, reaction occurs initially between individual macromonomers and then between macromonomers and HyperMacs comprising only a few macromonomers. The onset of the rapid increase in MW 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 MW species. The emergence of these ‘‘super’’ HyperMacs towards the end of the second phase can be seen in the SEC traces (Figure 3). The SEC trace 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,

Table 1.
Molecular weight and polydispersity data for HyperMac synthesized from an AB_2 macromonomer, where ‘A’ is bromine. Coupling reaction carried out in DMF, at 40 °C.

Time/hours	M_n/g mol^{-1}	DP_n	M_w/g mol^{-1}	DP_w	PDI
0	28,000	1.0	28,600	1.0	1.02
0.5	61,300	2.2	103,300	3.6	1.7
1	109,400	3.9	231,400	8.1	2.1
1.5	161,800	5.8	483,900	16.9	3.0
2	296,700	10.6	1,406,000	49.2	3.5
2.5	419,800	15.0	1,465,000	51.2	3.5
3	462,400	16.5	1,774,000	62.0	3.8
4	473,400	16.9	1,756,000	61.4	3.7
5	496,200	17.7	1,877,000	65.6	3.8
6	471,100	16.9	1,792,000	62.7	3.8
8.5	525,100	18.75	1,790,000	62.5	3.4

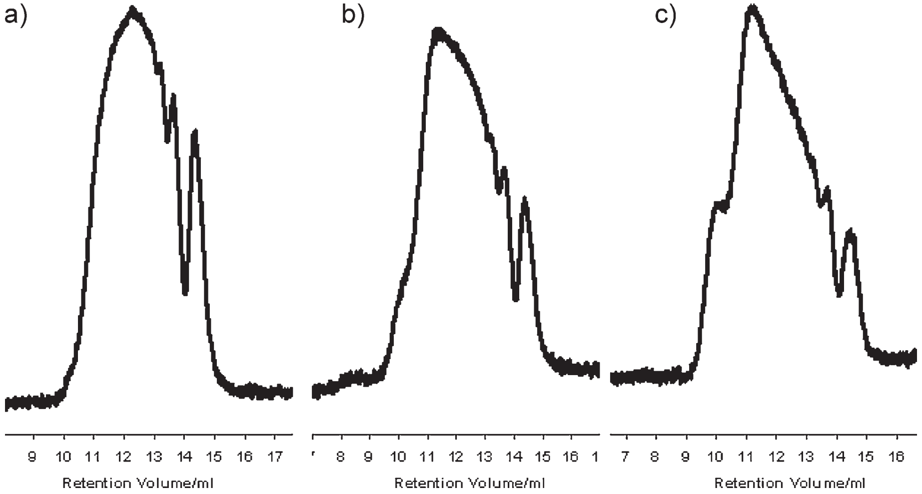

Figure 3.
SEC traces (RI trace) of HyperMac coupling reaction carried out at 40 °C for a) 90 minutes, b) 120 minutes and c) 240 minutes.

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 MW starts to increase dramatically.

The SEC trace obtained after 2 hours (Figure 3b) shows the molecular weight distribution (MWD) 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 that 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 MW. 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 MW "super" HyperMacs. The data in Figure 2 suggest that, after 4 hours, the coupling reaction is into the final phase where the MW plateaus. We believe that this plateau arises for two reasons. Firstly, we suspect that the rate of reaction does dramatically drop. The very high MW 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, resulting in a concomitant drop in the rate of reaction. However, the data in Figures 1,2 and 3 and Table 1 are derived from SEC analysis, and, as such, only inform us about the soluble fraction. As previously mentioned, the later samples had a significant fraction of insoluble gel which was removed by filtration prior to SEC analysis. It is inevitable that this gel fraction would have a higher MW than the sol fraction described above. A discussion of the sol-gel fraction analysis follows.

Further SEC analysis reveals (qualitatively) more information about how exactly high the MW gets for these 'super' HyperMacs. A plot of the normalized weight fraction versus log MW for the same HyperMac discussed above is shown as Figure 4. Approximate values of M_n, M_w and M_z are indicated in Figure 4 and a shoulder corresponding to the 'super' HyperMacs appears at a log MW value of approximately 6.7, corresponding to a value

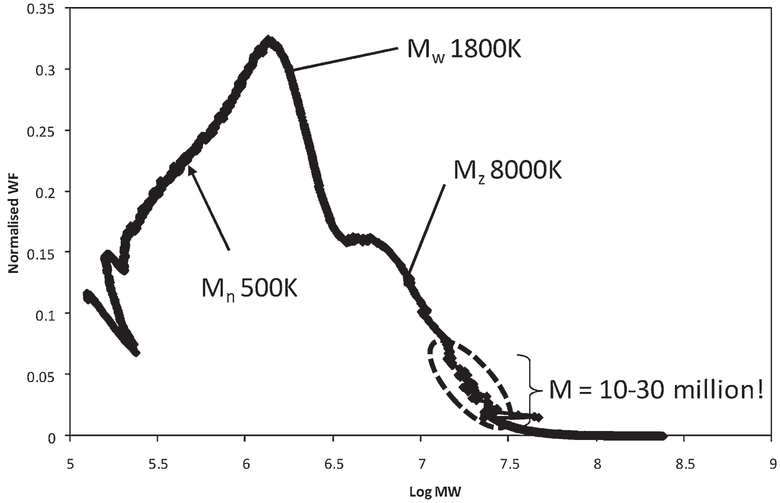

Figure 4.
Normalized weight fraction vs. log MW for HyperMac prepared from polystyrene AB_2 macromonomer of M_n 28,000 g mol^{-1}.

of MW = 5.0 million g mol^{-1}. Remarkably, a modest but significant weight fraction of this sample appears with a value of log MW between 7.0 and 7.5, corresponding to a MW of between 10 and 32 million g mol^{-1}! We accept that there will undoubtedly be errors associated with these values arising from the low concentrations of material and the fact that we have used a RALLS detector, which uses an angular correction for the asymmetry of light scattering for polymer chains of this size.[37] However, there is little doubt that a significant proportion of the (soluble) MWD will have a MW above 10 million g mol^{-1}.

Sol-Gel Fraction Calculations

In order to ascertain the weight fraction of insoluble gel in the HyperMac sample, sol-gel extraction measurements were carried out. Approximately 5 mg of dry HyperMac was weighed into a 10 mL volumetric flask which was filled to the mark with THF and sealed. This was repeated to give five such flasks in total. The flasks were placed on a rotating roller for a period of one week. After this time, the flasks were allowed to settle before samples of the liquor were removed for SEC analysis. The concentration of the sol fraction in solution was calculated from the refractive index detector and the results are shown in Table 2. Each sample was run in duplicate with a blank solvent sample run between sample runs. To ascertain the accuracy of these measurements, a similar experiment was carried out with a polystyrene standard (MW 66,000 g mol^{-1}) of

Table 2.
Sol and gel fractions determined using SEC for a HyperMac prepared from polystyrene AB_2 macromonomer of M_n 28,000 g mol^{-1}.

Sample Number	Mass HyperMac in 10 mL THF (mg)	Conc of soluble HyperMac (mg mL^{-1})	Sol Fraction	Gel Fraction
1	5.1	0.425	0.833	0.167
2	4.7	0.406	0.864	0.136
3	5.1	0.453	0.888	0.112
4	6.6	0.588	0.890	0.110
5	7.0	0.589	0.841	0.159

known concentration which showed 100% polymer solubility/recovery.

The data in Table 2 indicate that between 11 and 17% (by mass) of the polystyrene HyperMac was insoluble. This method of estimating sol/gel fractions is not without its errors. The polymer solutions are relatively dilute and the MWD broad. Under these conditions, deciding where the signal from the refractive index detector stops and the baseline starts is subjective. However, while there is a spread of results, these experiments do show unequivocably that a significant proportion of the polymer did not dissolve sufficiently to allow it to pass through the SEC. Indeed, fragments of insoluble, swollen gel could be seen floating in the polymer solution prior to analysis.

Conclusion

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 the 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/Cs_2CO_3 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. Furthermore, SEC analysis shows that such is the efficiency of the coupling reaction that a modest but significant portion of (the soluble fraction of) these HyperMacs has a MW in excess of 10 million $g\,mol^{-1}$. The soluble fraction is accompanied by an average of 13.7% of insoluble gel-like polymer.

The defining characteristics of a network are unequivocable! Networks are cross-linked, three-dimensional structures which, while they will swell, are insoluble even in a good solvent for the constituent polymer chains. HyperMacs are clearly NOT networks. The polymerisation of an AB_2 (macro)monomer is extremely unlikely to reach such extents of reaction that all of the molecules become interconnected. However, if one considers (i) that as one approaches the gel point during network formation the MW of the polymer chains tends to infinity, (ii) that during the synthesis of HyperMacs a notable weight fraction of the (soluble) polymer chains have a MW in excess of 10 million $g\,mol^{-1}$, and (iii) on average 13.7% of the HyperMacs is insoluble gel, it becomes clear that, in this case, the efficiency of the HyperMac polymer synthesis is so high that the polymer is approaching the gel point!

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