HyperMacs: Highly Branched Polymers Prepared by the Polycondensation of AB_2 Macromonomers, Synthesis and Characterization

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ABSTRACT: 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 (condensation) macromonomers with molecular weights from 3500 to 38 000 g mol^{-1}, which are then converted via a one-pot polycondensation reaction into high-molecular-weight, long-chain (hyper)-branched architectures. Because 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 macromonomers, the optimal conditions for the polycondensation reaction, and some preliminary characterization studies.

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 polymerization 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 utilizes 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.

Dendrimers were first synthesized in the 1980s via a step-growth condensation reaction of AB_x monomers, and numerous examples have been reported, including aliphatic[17] and aromatic polyesters,[18,19] aliphatic[20] and aromatic polyethers,[21−23] polyalkanes,[24,25] polysilanes,[26] and many more. Early work concentrated on the preparation of perfectly monodisperse dendrimers, and while these have some very interesting material properties, their synthesis is elaborate and very time-consuming. To obtain material rapidly and in large quantities, the condensation of AB_x monomers in a one-step process was developed.[27−29] These hyperbranched polymers are more polydisperse than dendrimers and have inherent defects in the form of built-in linear segments and unreacted functional groups but are still very highly branched.

We describe here a strategy to 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. Two groups to our knowledge have made hyperbranched polymers using AB_2 monomers that introduce a short linear spacer unit between branch points; Hawker[30] synthesized hyperbranched polyesters from monomers containing up to 5 units of ethylene glycol, and Feast[31] similarly prepared hyperbranched polyesters with short linear $(CH_2)_x$ units between branch points where $x = 2-4$. 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 g mol^{-1}; although this offers the possibility of varying the molecular weight between branch points from below the entanglement molecular weight, M_e, to many times M_e, the imperfect nature of the branched structure produced by the polycondensation 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 mac-

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romonomers is also feasible, making this a very versatile methodology.

There are numerous examples in the literature of coupling reactions that could be exploited to synthesize HyperMacs, for example, esterification,[17−19] Williamson reaction between an alkoxide and a halide to yield an ether linkage,[20−23] and Suzuki coupling reaction between a boronic acid and a halide.[27−29] We have used a Williamson coupling reaction to yield an ether linkage in a fashion similar to that used by Fréchet in the synthesis of classical hyperbranched and dendritic polyethers.[21,22,34] 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.

Although the resulting polymers are not perfectly branched, one intriguing possible application of this methodology is to synthesize "model" systems for molecular rheology. The rheology of polymer melts may be tailored by controlled addition of long-chain branches using "open-site" metallocene catalysts,[32] and the molecular mechanism of vinyl-group reincorporation leads statistically to the same one-parameter topological family of branched structures as the "AB_2" polycondensation described here,[33] the only difference lying in the exponential polydispersity of the molecular weight between branches in the case of the metallocene-catalyzed system. An entangled model system intermediate between the doubly random ensemble of the metallocene catalyzed 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. The ability to synthesize HyperMacs, in which the linear polymer chain between branch points can be varied by controlling the molecular weight of the macromonomer, will enable a "tuning" of molecular parameters of the branched polymers and facilitate their use in structure property correlation studies.

Experimental Section

Materials. Benzene (HPLC grade, Aldrich) and styrene (Aldrich) were both dried and degassed over CaH_2 (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 synthesized in two steps from dihydroxybenzophenone according to the procedure of Quirk and Wang.[34] 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.[35] 18-Crown-6-ether and potassium carbonate powder, 325 mesh (both Aldrich), were dried in a vacuum oven and stored in a vacuum desiccator.

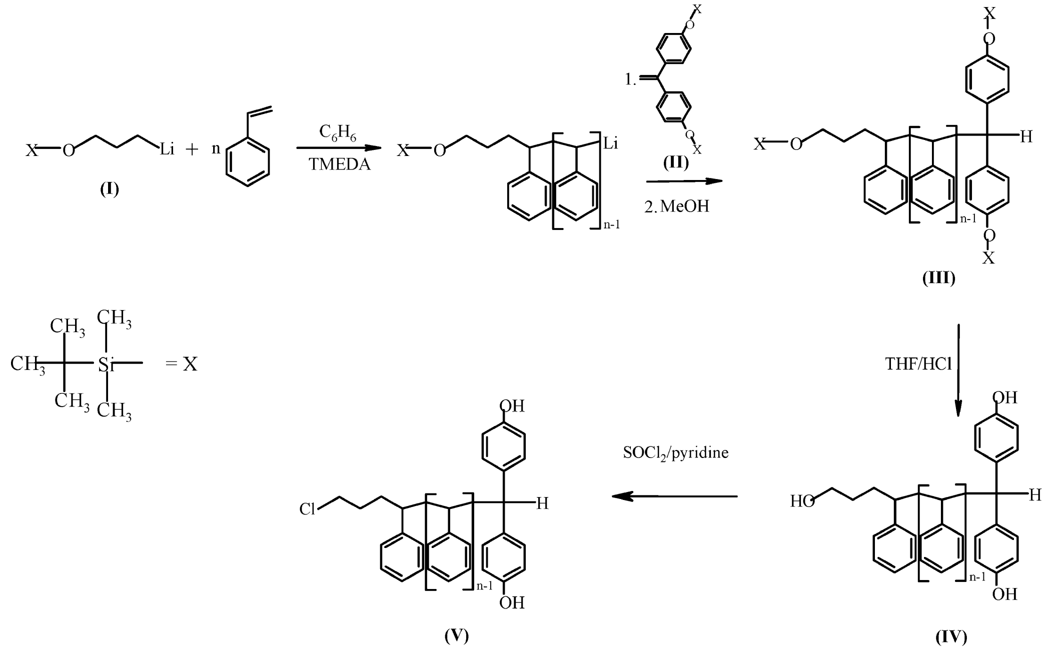
Measurements. Molecular-weight analysis was carried out by size exclusion chromatography (SEC) on a Viscotek TDA 302 with refractive index, viscosity, and light scattering detectors. A value of 0.185 (obtained from Viscotek) was used for the d*n*/d*c* of polystyrene. PLgel 2 × 300 mm 5-μm mixed-C columns (with a linear range of molecular weight from 200 to 2 000 000 g mol^{-1}) were employed, and 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 analyzed by SEC using a Viscotek 200 with a refractive index detector and PLgel 3 × 300 mL 5-μm 10^4-Å high-resolution columns (with an effective molecular weight range of 10 000−600 000 g mol^{-1}), and THF was used as the eluent at a flow rate of 1.0 mL/min. ^1H 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. Benzene (500 mL) and styrene (50 g, 0.48 mol) were distilled, under vacuum, into a 1-liter reaction flask. To the monomer solution was added tetramethylethylenediamine (TMEDA), 1 mole equiv 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 g mol^{-1}, we used 0.755 mL (5 mmol) of TMEDA and 7.14 mL of initiator (5 mmol). Upon addition of the initiator to the reaction mixture, the orange-red color of living polystyryllithium was observed. The solution was stirred for 1 h 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 equiv with respect to 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 g mol^{-1}, M_w 12 900 g mol^{-1} Pd 1.04. ^1H 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 dropwise concentrated HCl (37 wt %), mole ratio of acid/protected alcohol was 5:1. The solution was then warmed 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 2 days. Yield >95%. ^1H 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 g mol^{-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 was stirred for 15 min 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 min 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 ^1H 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

Scheme 1. Synthesis of AB_2 Polystyrene Macromonomer



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 varied, a typical polycondensation coupling reaction was carried out thus: 2 g of AB_2 macromonomer 3 (M_n 12 400 g mol^{-1}, 1.6 x 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 was 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 h. 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 56 200 g mol^{-1}, M_w 167 400 g mol^{-1}, PDI 3.2.

Results and Discussion

Anionic polymerization is a living polymerization technique with no intrinsic termination reaction and produces polymers of well-defined molecular weight and narrow polydispersity. The living nature of the polymerization also 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 primary 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 can be used to build up novel, highly branched polymeric architectures. The macromonomers are joined together by via an ether linkage formed by a Williamson coupling reaction.

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. Our first attempt to synthesize such an AB_2 macromonomer involved the use of an initiator derived from the reaction of 1,1-bis(4-*tert*-butyldimethylsiloxyphenyl)ethylene (**II**) with *sec*-butyllithium. This diphenylhexyllithium derivative initiator was successfully synthesized in benzene and did initiate the polymerization of styrene, but the resulting polymers were not well-defined. Although observations in the literature[36] suggest that diphenylalkyllithiums, either unsubstituted or with electron donating substituents on the aromatic ring, can function as effective initiators for the anionic polymerization of styrene, diene, and methacrylate monomers to generate polymers with predictable molecular weights and relatively narrow molecular weight distributions, we did not find this to be the case. When aiming for a molecular weight (M_n) of 5000 g mol^{-1}, the actual molecular weight of the polymer was 8000 g mol^{-1} and the polydispersity was 1.2. The reason for this is that the rate of initiation was slow with respect to the rate of propagation. Slow initiation is not uncommon in anionic polymerization, *n*-butyllithium for example gives similar or worse results than the initiator mentioned above, with polydispersity values as high as 1.5. The cause in the case of *n*-BuLi is the high aggregation state of the initiator in hydrocarbon solvents and can be rectified by the addition of Lewis bases such as ethers and amines.[36] In the case of the diphenylhexyllithium derivative, the reason for slow initiation is not a high aggregation state. This type of lithium species exists in dimeric form in hydrocarbon solvents (cf. *n*-Buli which exists predominantly as a hexamer), and as such, addition of Lewis base has no effect on the rate of initiation. The presence of two phenyl rings bonded directly to the carbanion reduces the nucleophilicity of the initiator, thereby making it less reactive. In fact, the addition of diphenylethylene to a polymer synthesized by anionic polymerization and initiated with a lithium initiator is a well-documented way of reducing the activity of the propagating site.[36]

In light of this problem, the strategy was changed, and it was decided to use 1,1-bis(4-*tert*-butyldimethylsiloxyphenyl)ethylene to end cap the living polymer; diphenylethylene (DPE) derivatives will quantitatively end cap polystyryllithium with only a single DPE moiety because the DPE group is too sterically bulky to propagate. A commercially available initiator, 3-*tert*-butyldimethylsiloxy-1-propyllithium, was subsequently used in all polymerizations (see Reaction Scheme 1).

Because this initiator is an *n*-alkyllithium species, in the absence of any Lewis base additive, the rate of initiation is slow with respect to propagation, and the resulting polymers have a polydispersity of 1.3−1.5. Early polymerizations initiated by 3-*tert*-butyldimethylsiloxy-1-propyllithium with triethylamine (TEA) as the Lewis base additive failed. With 1 equiv of TEA (with respect to Li), initiation was slow, the orange color of living PSLi evolving over several minutes, the target M_n was 10 000 g mol^{-1}, but the actual M_n of the resulting polymer was 19 000 g mol^{-1} and the polydispersity 1.4. With 5 equiv of TEA, initiation appeared to be reasonably quick, as indicated by the evolution of the orange color of living PSLi within a minute, but the polymerization was still not well-controlled. Again, the target M_n was 10 000 g mol^{-1}, but the actual M_n was 25 000 g mol^{-1} and the polydispersity of the resulting polymer was 1.5. With 10 equiv of TEA, there was no initiation at all. TEA as an additive in the polymerization of styrene with *n*-BuLi as the initiator usually results in well-defined polymers with narrow molecular weight distributions.[36] We have not ascertained what the cause of this TEA/3-*tert*-butyldimethylsiloxy-1-propyllithium initiator problem is, but we are continuing to investigate. However, the addition of as little as 1 equiv of TMEDA as the Lewis base additive is sufficient to break up the alkyllithium aggregates, increase the rate of initiation, and lower the polydispersity to 1.05. The polymers initiated with 3-*tert*-butyldimethylsiloxy-1-propyllithium were end capped with 1,1-bis(4-*tert*-butyldimethylsiloxyphenyl)ethylene, **II** (Reaction Scheme 1), to yield the fully protected AB_2 macromonomer **III**. Because this DPE derivative is known not to propagate[36] because of its steric bulkiness and reduced reactivity, it is possible to add an excess of this reagent with respect to lithium to facilitate this end-capping reaction. Even so, this is a slow reaction, and the mixture was stirred for 5 days[34] 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. ^{1}H NMR analysis of the macromonomer shows that the degree of end capping, as evidenced by the presence of the TBDMS protection groups, was practically quantitative (see Figure 1), which shows the ^{1}H NMR spectrum of a macromonomer **III** (3, M_n 12 400 g mol^{-1}) in which all the protection groups are intact**.** The region at 0.0 ppm has been expanded to show the signals for the C**H**$_3$-Si protons of the protection groups. The signal at 0.0 ppm corresponds to the protection group introduced by the initiator and, therefore, is present in every chain, and the signal at 0.1 ppm corresponds to the protection groups introduced by the end-capping reaction. For a quantitative end-capping reaction, the ratio of these two signals should be 2:1; the integration values for these two peaks indicate that greater than 97% of chains have been successfully end capped.

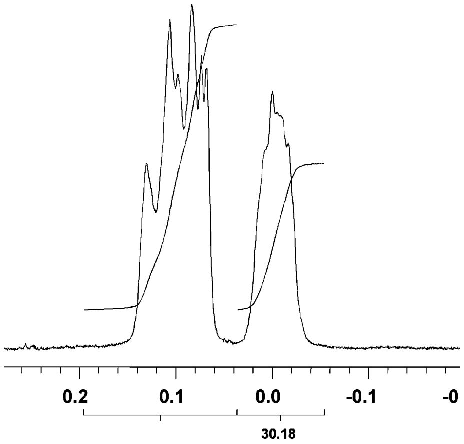


Figure 1. ^{1}H NMR of protected macromonomer 3, M_n 12400 g mol^{-1} (III, Scheme 1) showing signals for Si−(C**H**$_3$)$_2$ at 0.0 ppm for protected alcohol introduced at the initiating end of chain and at 0.1 ppm for protected phenols introduced by end-capping reaction. Ratio of integrals indicates practically quantitative (>97%) end-capping by DPE derivative.

The TBDMS protection groups were removed by acid hydrolysis[34] 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_2OSi) to 3.15 ppm (CH_2OH) **(**see Figure 2 inset**),** confirming complete deprotection of all the alcohol groups. Furthermore, after deprotection, a signal for the phenolic O**H** becomes apparent at 3.7−3.8 ppm (Figure 2); this signal disappears on shaking with D_2O. Analysis of the integrations of the phenolic hydroxyl protons indicates 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.

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.[37] ^{1}H NMR was used to follow this transformation; the broad signal at 3.15 ppm of the −C**H**$_2$-OH completely disappears, to be replaced with a new broad signal at 2.9 ppm, corresponding to −C**H**$_2$-Cl (see Figure 2 inset). Analysis of the integration ratio of −C**H**$_2$-Cl versus the signal for the polystyrene aromatic protons (δ 6.2−7.2 ppm) confirms quantitative functionalization. It is necessary to carry out the ^{1}H NMR analysis of these transformations in C_6D_6 rather than $CDCl_3$ as, in the latter solvent, the signals from the starting material and products of

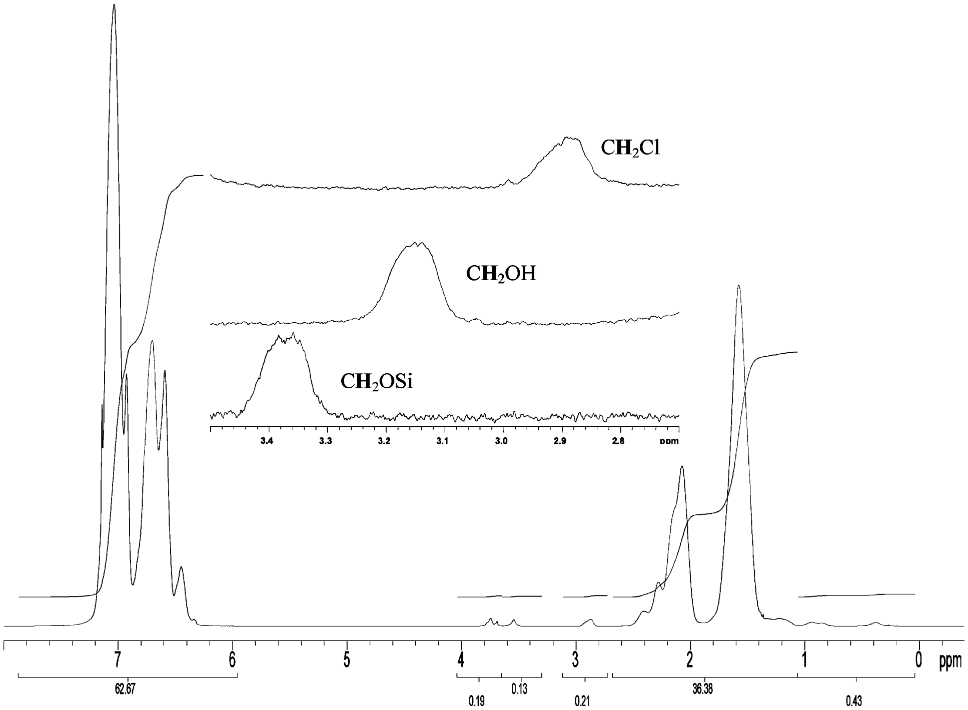


Figure 2. ^{1}H NMR (C_6D_6) of macromonomer 3 M_n 12400 g mol^{-1}. Inset: transformation of end group introduced at the initiating end of chain from protected alcohol ($\mathbf{CH_2}$–O–Si) to primary alcohol ($\mathbf{CH_2}$–OH) to alkyl chloride ($\mathbf{CH_2}$–Cl), macromonomer 3.

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/g mol^{-1}	M_w/g mol^{-1}	Pd
1	3600	3800	1.06
2	6300	6500	1.04
3	12400	12900	1.04
4	16800	17200	1.02
5	37300	38900	1.04

these reactions are not sufficiently resolved. A series of five AB$_2$ macromonomers have been prepared with molecular weights in the range 3500–38 000 g mol^{-1} as shown in Table 1.

Synthesis of HyperMacs. Hyperbranched polymers, synthesized 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. A generic and hypothetical example of the type of structure that might be expected from such a polycondensation is shown in Scheme 2. One further "defect" that may arise as a result of these polycondensations is loop formation as a result of intramolecular cyclization, not shown in Scheme 2.

A Williamson coupling reaction to form an ether linkage has been used in the polycondensation, and because 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. Because the macromonomer coupling reaction will be promoted when carried out in a good solvent for the polymer and Feuer and Hooz[38] suggest that ether formation is favored (and C alkylation minimized) 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 favored in more dilute solutions, and therefore, we might expect lower-molecular-weight products under these conditions. However, we might also expect that the coupling reactions will be retarded by very high solution concentrations in which the viscosity will be high and stirring difficult. Fréchet[21] mentions that vigorous stirring was important in his work on the synthesis of dendrimers using a Williamson coupling reaction, presumably because the potassium carbonate (used as a base to deprotonate the phenolic alcohol) is insoluble in the solvents used, and in the absence of good stirring, the base will not be intimately mixed with the other reactants. 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 macromonomer 5 (M_n 37 300 g mol^{-1}) in refluxing DMF are shown in Table 2 and Figure 3.

It can be seen that this polycondensation coupling reaction proceeds rapidly and appears to have virtually reached its end point within 4 h. Furthermore, it should be noted that M_n grows more slowly than M_w and this divergence is further demonstrated by the increasing

Scheme 2. Synthesis of HyperMac from Polystyrene AB_2 Macromonomer

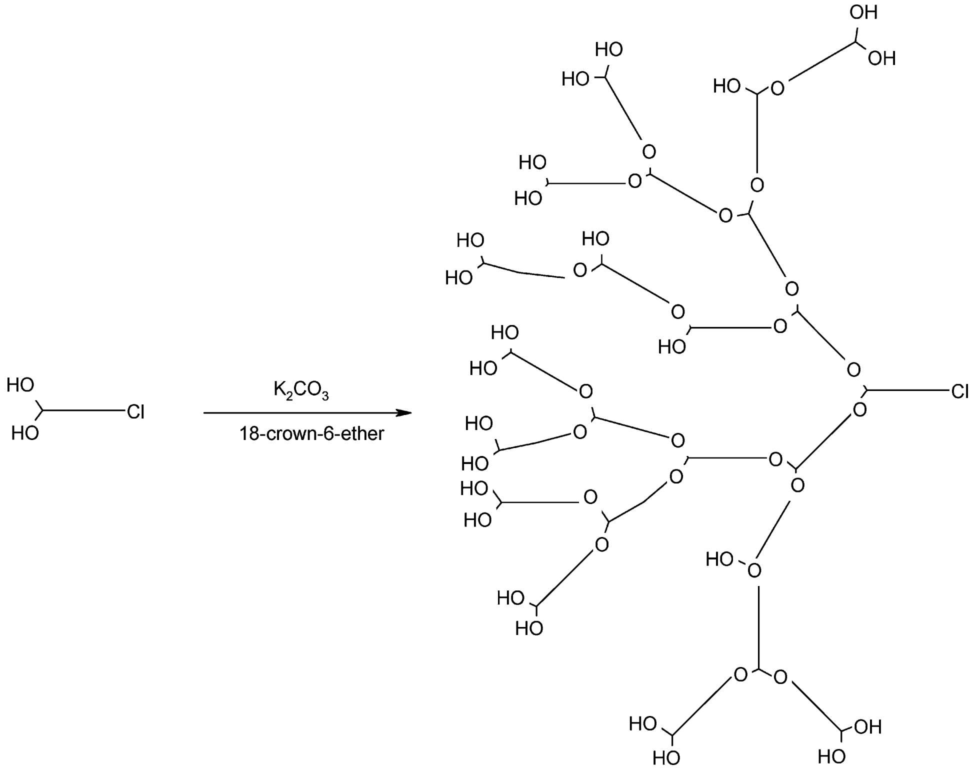


Table 2. Molecular Weight, Polydispersity, and Intrinsic Viscosity Data for HyperMac Synthesized from Macromonomer 5

time/hours	M_n/g mol^{-1}	M_w/g mol^{-1}	PDI	$[\eta]_{hyper}$/dl g^{-1} [a]	$[\eta]_{lin}$/dl g^{-1} [b]	g' [c]
0	37300	38900	1.04	0.23	0.24	
1	76500	136000	1.8	0.46	0.59	0.78
2	143000	391000	2.7	0.80	1.24	0.65
4	176000	502000	2.9	0.90	1.48	0.61
20	185000	556000	3.0	0.94	1.58	0.59

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

polydispersity with time. This behavior is expected and typical for the polycondensation of AB_2-type monomers. The molecular weight of the final product indicates a number-average degree of polymerization of the macromonomer, Dp_n, of approximately 5 and a weight-average degree of polymerization, Dp_w, of 14. While these reactions have undoubtedly worked, the extent of reaction is maybe not as high as we might have hoped. However, there are a number of probable reasons for this. As previously discussed, there is sure to be a certain amount of undesirable intramolecular coupling, and this evident in Figure 3. SEC analysis of this reaction (using high-resolution columns) shows the conversion of the macromonomer (starting material), retention volume 23 mL, into dimer, trimer, tetramer, pentamer, and eventually higher molecular material. SEC also shows the emergence of a shoulder on the peak for the starting material at slightly higher retention volumes. It is almost certain that this peak at higher retention volumes and therefore smaller hydrodynamic volume is the cyclized macromonomer formed as a result of intramolecular coupling, it being well-known that cyclic polymer chains have a smaller hydrodynamic volume than that of their linear analogues.[39] There is also evidence of a similar shoulder on the peak corresponding to the “dimer”, and it is likely that cyclization will occur across the full molecular weight distribution.

Another possible limiting factor, especially on the rate of the polycondensation, is the viscosity of the solution. At the end point of this reaction, the M_w is over 500 000 g mol^{-1}, and the viscosity of a 20% solution of this polymer is high. These small scale reactions are stirred with a magnetic stirrer bar that, as the reaction proceeds, may no longer be generating good mixing between all the reactants. A final likely limiting factor is the affect 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 catalyzed by acidic or basic materials.[40] 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, 5.4×10^{-3} mol/dm^3 in this reaction. The likelihood of deleterious side reactions is supported by ^1H NMR analysis (Figure 4) of a HyperMac formed by such a polycondensation. Figure 4 shows the area of the spectrum in which one would expect to see any unreacted alkyl chloride (δ 2.9 ppm) or phenol (δ 3.7–3.8 ppm) functionality (see Figure 2). Clearly, there is no evidence of residual alkyl chloride groups, and it is doubtful that residual phenol groups remain at the end of the reaction. Because it has been estab-

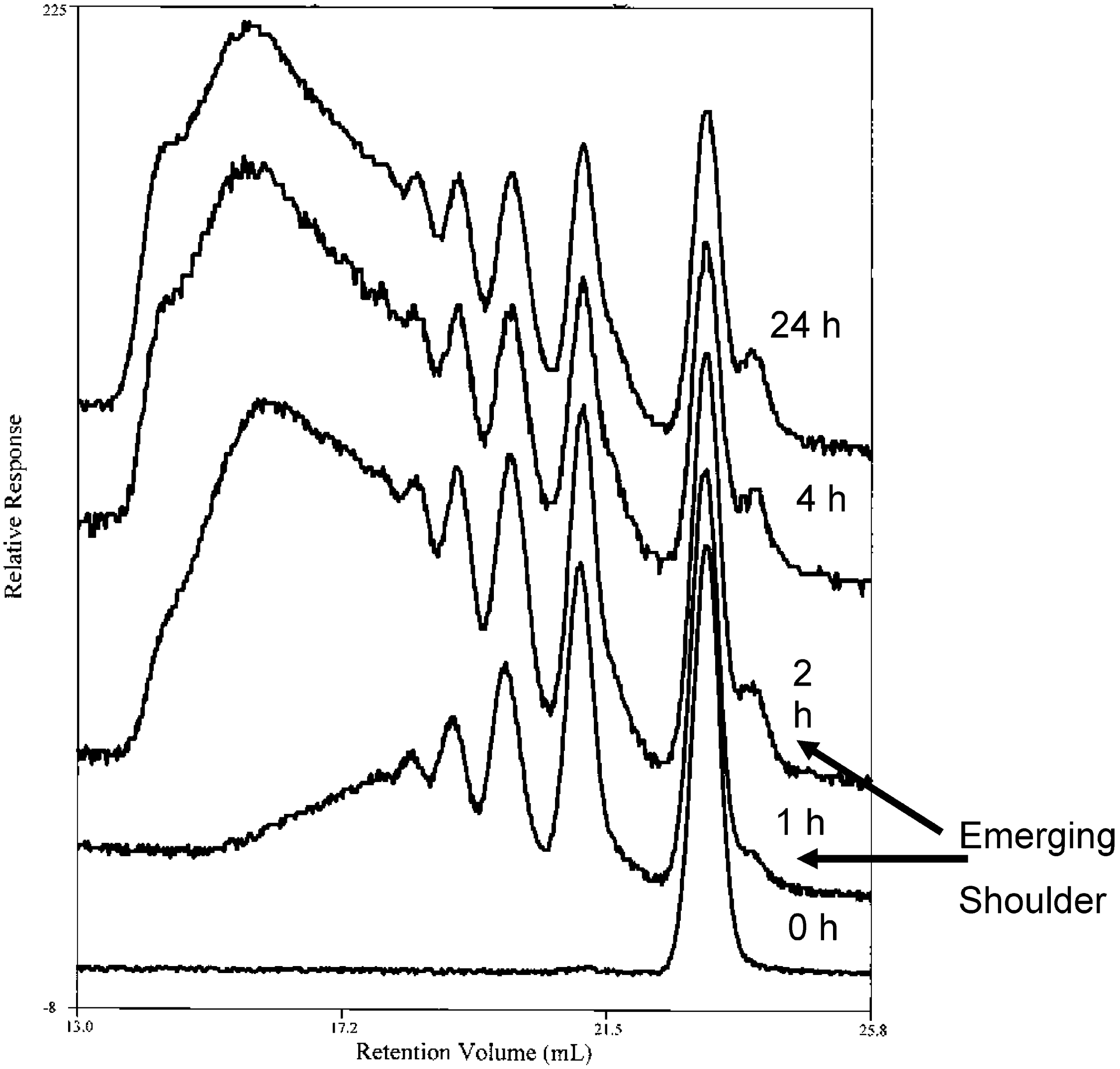


Figure 3. SEC (RI detector) chromatogram (using 3 × 300 mL PLgel 5 μ 10^4 Å high-resolution columns) showing, for the polycondensation of macromonomer 5, how the molecular weight of the resulting HyperMac increases with time and the emergence of a shoulder at 23−24 mL, indicating cyclization of the macromonomer by an intramolecular reaction.

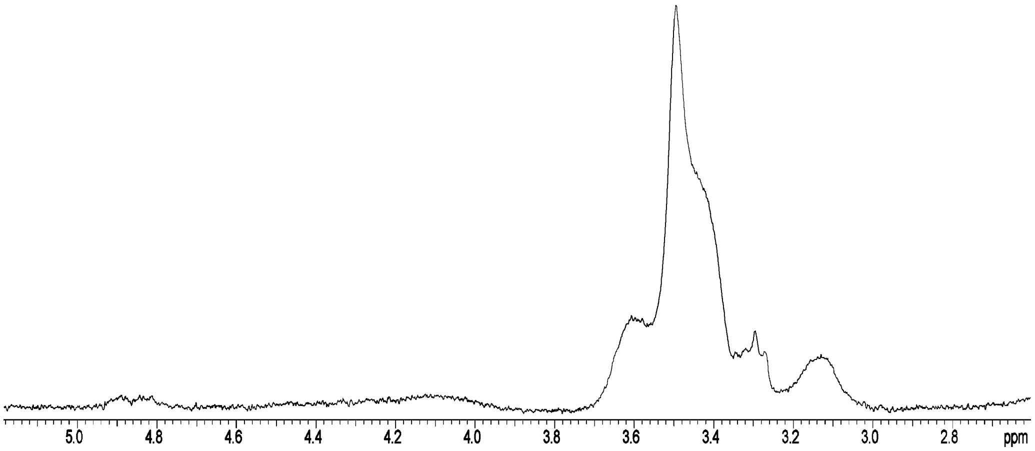


Figure 4. ^{1}H NMR of HyperMac formed by the polycondensation of macromonomer 3, M_n 12400.

lished that both functionalities are present at practically quantitative levels in the macromonomers and that the reaction product of the polycondensation contains some uncoupled polymer, it is likely that side reactions have occurred. The peaks that are present in the region from 3 to 3.7 ppm in Figure 4 are likely to arise from several overlapping signals. The predominant signal is likely to be the C**H**$_2$OPh ether linkage formed by the successful Williamson coupling reaction; the signal at 3.5−3.6 ppm may be ascribed to the **H**C(Ph)$_2$ of the DPE end group. The remaining signals may represent the reaction products of the side reactions.

To verify that the product does in fact have a branched architecture and to get some idea of the degree

Table 3. Molecular Weight, Polydispersity, and Intrinsic Viscosity Data for HyperMacs Synthesized from Macromonomers 1−5

macromonomer	M_n/g mol^{-1}	Dp$_n$	M_w/g mol^{-1}	Dp$_w$	PDI	$[\eta]_{hyper}$/dl g^{-1a}	$[\eta]_{lin}$/dl g^{-1b}	g'^c
1 (3600 g mol^{-1})	16100	4.5	36600	9.6	2.2	0.15	0.23	0.65
2 (6300 g mol^{-1})	33600	5.3	65400	10.1	1.9	0.23	0.34	0.67
3 (12400 g mol^{-1})	52600	4.2	167000	13.0	3.2	0.42	0.67	0.63
4 (16800 g mol^{-1})	88000	5.2	298000	17.3	3.4	0.57	1.01	0.56
5 (37300 g mol^{-1})	185000	5.0	556000	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] $g' = [\eta]_{hyper}/[\eta]_{linear}$.

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.[16,41] Shown in Table 2 is the development of intrinsic viscosity of the HyperMac, $[\eta]_{hyper}$, 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 $K = 12.8 \times 10^{-5}$ 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 because 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 $[\eta]_{hyper}$ and $[\eta]_{linear}$ 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 because the intrinsic viscosity of the HyperMac is of a material that 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 is work in progress and will be reported at a later date. Despite that caveat, the low values of g' undoubtedly confirms that this HyperMac is highly branched.

The results of four analogous polycondensation reactions of macromonomers 1, 2, 3, and 4 with molecular weights of 3600, 6300, 12 400 and 16 800 g mol^{-1}, respectively, are shown in Table 3.

In each case, the concentration (w/v) of macromonomer solution and relative quantities of polymer, potassium carbonate, and crown ether were the same as previously described for the polycondensation of macromonomer 5. In each case, the polycondensation was successful, and polymers with branched architectures were formed. When the data for the HyperMac synthesized from the highest molecular weight macromonomer, 5, is also considered, it would 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 five 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. It should also be noted that the rate of the reaction and, therefore, the time at which each polycondensation reaches an end point also varies with the molecular weight of macromonomer. As previously discussed, the polycondensation of macromonomer 5 took over 4 h to reach an end point, although little change was observed after 4 h. As the molecular weight of the macromonomer decreases, so do the times required to reach an end point in the polycondensation, with macromonomers 3 and 4 requiring approximately 90 and 120 min, 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. The branching factor g' seems to be lower for HyperMacs made from the higher-molecular-weight macromonomers, although, in each case, the value of g' falls within a fairly narrow range (0.56−0.65). The values compare very favorably 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 poly(methyl methacrylate), respectively. 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. We will discuss in more detail the branching factors and compare the data obtained for a fractionated HyperMac with values obtained in the literature for various branched architectures in a subsequent publication.

Careful analysis of the SEC data for the five HyperMacs reveals that the degree of polycondensation is, not surprisingly, closely correlated with the relative amount of “unreacted” macromonomer, and by “unreacted” we mean the combined amounts of uncoupled macromonomer and cyclized macromonomer, the former probably arising from reaction of the alkyl chloride functionality with dimethylamine impurity in the DMF and the latter formed as a result of an intramolecular coupling reaction. In the case of the HyperMac with highest degree of polycondensation, from macromonomer 4, the “unreacted” macromonomer accounts for just 9.4% of the total mass of product (as estimated from relative area under the refractive index chromatogram), whereas, in the case of the HyperMac with the lowest Dp$_w$ from macromonomer 1, the “unreacted” polymer accounts for 13.4%. More interestingly, though, is the make up of this “unreacted” material. While attempts to deconvolute the peaks generated by uncoupled and cyclized macromonomer are hampered by the relatively small differences in hydrodynamic volume, it is possible to estimate the proportion of cyclized polymer in each case, and a clear trend emerges with respect to molecular

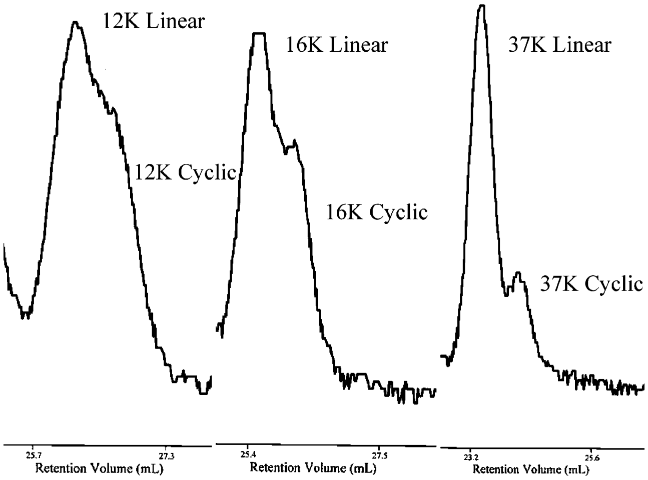


Figure 5. SEC (RI detector) chromatogram (using 3 × 300 mL PLgel 5 μ 10^4 Å high-resolution columns) showing relationship between degree of cyclized macromonomer formed by intramolecular coupling and molecular weight of macromonomer.

weight of macromonomer, see Figure 5. The proportion of cyclized macromonomer increases with decreasing molecular weight of macromonomer.

For the HyperMac synthesized from macromonomer 5 (M_n 37 300), only 24% (estimated from the peak heights/areas of the refractive index chromatogram) of the “unreacted” material is cyclized; this value increases to 39 and 41% for the HyperMacs made from macromonomers 4 (M_n 16 800) and 3 (M_n 12 400), respectively. In the case of the samples from macromonomers 1 and 2 (M_n 3600 and 6300, respectively) the peaks for the linear and cyclic macromonomer are not sufficiently resolved to allow an accurate estimate, although the quantity of cyclized macromonomer appears to be greater than 50%. The SEC traces in both of these cases show the peak for the “unreacted” macromonomer is significantly broader than the peak for the starting macromonomer and that it seems to broaden to higher retention volumes. This would tend to suggest that there are two unresolved peaks, probably of similar intensity. It, therefore, seems certain that, under these reaction conditions (20% w/v), the lower-molecular-weight macromonomers are more prone to intramolecular cyclization than the higher-molecular-weight macromonomers, and it is also highly likely that the intramolecular reaction is not restricted to the starting material. The extent of cyclization of a given macromonomer may be indicative of the degree of intramolecular coupling in any given polycondensation. In summary, it would seem that reactions with impurities and intramolecular cyclization are far more important than viscosity as limiting factors and that the increasing degree of cyclization of the lower-molecular-weight macromonomers may be the cause of the slightly lower extent of polycondensation of these HyperMacs.

The Influence of Solution Concentration. In light of the above findings on the occurrence of cyclization, we investigated the influence of the concentration of the macromonomer solution on the extent of polycondensation with the aim of minimizing intramolecular reactions. A series of five polycondensations was carried out using macromonomer 3 (M_n 12 400 g mol^{-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 h; at 20%, this time had increased to 90 min, 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 analyzed by SEC, and the results are shown in Table 4 and Figure 6.

It can be seen from both the chromatograms and the analysis that concentration has a dramatic affect on the extent of polycondensation. The data in Table 4 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 leveling 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 example, extracted 1 h 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 because of thermal degradation. While 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 6), in which we can see that the make up of “unreacted” macromonomer changes significantly as the concentration increases.

The peak with a retention volume of approx 26−27 mL is bimodal, indicating the presence of both unreacted 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 behavior for the dimer. At 5%, this peak is clearly unsymmetrical and skewed toward higher retention volumes, indicating the presence of cyclized dimer, whereas, at 40%, the peak looks more skewed to lower retention volumes. However, 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

Table 4. SEC Characterization Data Showing the Effect of Solution Concentration on the Synthesis of HyperMacs Prepared Using Macromonomer 3

soln conc/% w/v	M_n/g mol^{-1}	Dp$_n$	M_w/g mol^{-1}	Dp$_w$	PDI	$[\eta]_{hyper}$/dl g^{-1}[a]	$[\eta]_{lin}$/dl g^{-1}[b]	g'[c]
5	35000	2.8	74600	5.8	2.1	0.26	0.38	0.68
10	40500	3.3	104000	8.1	2.6	0.32	0.48	0.67
20	52600	4.2	167000	13.0	3.2	0.42	0.67	0.63
30	57200	4.6	206000	15.9	3.6	0.45	0.78	0.58
40	75700	6.1	282000	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] $g' = [\eta]_{hyper}/[\eta]_{linear}$.

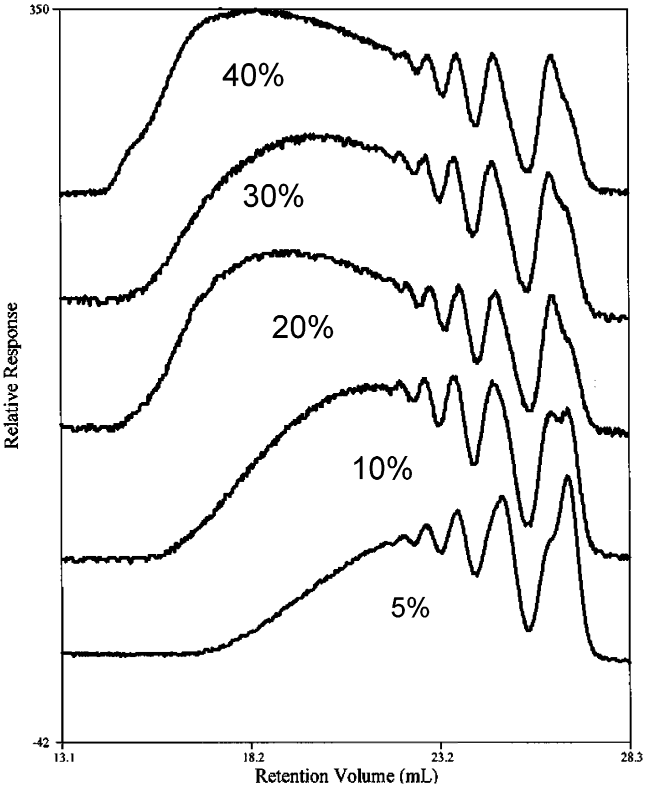


Figure 6. SEC (RI detector) chromatograms (using 3 × 300 mL PLgel 5 μ 10^4 Å high-resolution columns) showing affect of solution concentration w/v on extent of polycondensation and degree of cyclization. As the concentration of solution increases, the extent of polycondensation increases and the degree of cyclization decreases.

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 an increasingly compact, branched structure.

The Influence of Solvent. As we have already demonstrated, the polycondensation reaction occurs very rapidly in refluxing DMF, the reactions proceeding in a matter of a few hours but the extent of reaction may well be somewhat limited by side reactions between the macromonomer/growing HyperMac and impurities generated by heating DMF. With this in mind, we considered alternative solvents. As previously mentioned, the two principal requirements for a solvent for this reaction is that (a) the solvent is a good solvent for polystyrene and (b) that the solvent is aprotic with a high dielectric constant. These constraints somewhat limit the choice. Other solvents that meet requirement (b) include acetone, acetonitrile, and dimethylsulfoxide, all of which are nonsolvents for polystyrene. The "textbook" good solvents for polystyrene, toluene and benzene, both have very low dielectric constants, and therefore, the only other viable solvent we could investigate the use of was tetrahydrofuran (THF). We found, not surprisingly, that the rate of reaction in refluxing DMF was far higher than that in refluxing THF, not only because of the difference in temperature (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 favored by solvents with high dielectric constants.[39] In contrast to DMF, the reaction in THF did not proceed rapidly, after 150 min 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.

Conclusions

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. The successful synthesis of a series of AB_2 polystyrene macromonomer "building blocks" with molecular weights in a range from 3600 to 37 300 g mol^{-1} has been achieved by anionic polymerization, in which the polymerizations are initiated by a propyllithium species containing a protected primary alcohol functionality and end capped with a diphenylethylene derivative containing two protected phenol groups. Following deprotection and conversion of the primary alcohol to an alkyl chloride group, the macromonomers can be built up into highly branched structures by a polycondensation reaction involving a Williamson coupling reaction in DMF. 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 0.56–0.65, 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 impact of these two factors on the extent of the polycondensation reaction was related, to a small degree, on the molecular weight of the macromonomer, lower-molecular-weight macromonomers undergoing demonstrably higher levels of intramolecular coupling, leading to slightly lower degrees of polycondensation. However, it was found that the solution concentration had a much greater influence on the impact of these two limiting factors. At low solution concentrations, 5% w/v, the polycondensation reaction produced materials that 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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